MODERN ALCHEMY

MODERN ALCHEMY

BY

WILLIAM ALBERT NOYES
UNIVERSITY OF ILLINOIS

AND

W. ALBERT NOYES, JR.
BROWN UNIVERSITY

SPRINGFIELD · ILLINOIS BALTIMORE · MARYLAND

CHARLES C THOMAS

1932

PRINTED IN THE UNITED STATES OF AMERICA
BY THE GEORGE BANTA PUBLISHING COMPANY, MENASHA, WISCONSIN

Dedicated to

KATHARINE MACY NOYES

and

SABINE ONNILLON NOYES

PREFACE

For more than a thousand years alchemists sought in vain for the Philosopher's Stone, which should transmute base metals into gold and for an Elixir of Life, which should give eternal youth. The quest was finally abandoned as hopeless, but the transmutation of elements has been observed in recent times and many ways of healing disease and prolonging life have been found.

The vicissitudes of the search for transmutation and for healing principles are typical of the progress of science and have been taken as the ground work of this book.

In the first chapter, there is a superficial survey of the various branches of science and an attempt is made to discover their common characteristics. This is followed by an outline of modern ideas about the constitution of matter, given as an illustration of the scientific method in dealing with one of the most fundamental problems engaging the attention of scientific men and as a basis for the discussion of valence.

The consideration of the constitution of matter is chiefly from the point of view of the physicist or physical chemist with a mathematical background, while the chapter on valence is an attempt to apply the inductive methods of organic chemistry in gaining a better knowledge of the function of electrons in chemical combination.

The chapter on the effects of radiation on chemical action gives a general account of recent advances in a related field.

The chapter on new elements and new uses for old ones deals with topics closely related to the constitution of matter and chapters III and VII tell of actual transmutations of elements and methods for the healing and control of diseases.

It is hoped that the book, as a whole, may be of interest to readers trained in other sciences than chemistry as well as to chemists.

We wish to express our indebtedness to Dr. E. E. Slosson, who first suggested to us that we should write, together, a book of this general character.

We are also under obligation to a number of friends who have read the whole or a part of the manuscript and have made many helpful suggestions: especially to Farrington Daniels of Wisconsin, A. H. Compton, W. E. Vaughan and J. K. Senior of Chicago, Charles Zeleny and W. C. Rose of Illinois, E. A. Flood of Brown, Walter Goebel of the Rockefeller Institute, C. W. Balke of the Fansteel Products Co., North Chicago, T. Wright Wilson of Pennsylvania, and T. M. Lowry of Cambridge, England.

Roger Adams, Rosalie M. Parr, B. S. Hopkins, and S. W. Parr have assisted us by writing about topics with which they have a close acquaintance.

Urbana, Illinois
Providence, Rhode Island

CONTENTS

MODERN ALCHEMY

Chapter I

THE METHODS OF SCIENCE

I. Definition of Science

There is a tendency among some scientific men and especially among physicists and mathematicians, to claim that only knowledge which is the result of exact measurements and rigid mathematical reasoning can be called scientific. If we define science as that body of knowledge which is complete and so certain that we cannot believe it will change as new facts are discovered, such an attitude may be philosophically justified.

An examination of the historical development of any branch of science will convince an unprejudiced student that advances have not been made exclusively nor even chiefly by means of exact measurements and mathematical reasoning. At the foundation of all science is the assumption that we are part of an orderly universe and that the phenomena which we observe constantly repeat themselves in the same manner when the conditions are the same. Without this assumption, any attempt to acquire a knowledge of our surroundings would be hopeless. But even this simple assumption cannot be completely demonstrated and some people question it. No one has been able to cite a case in the realm of material things where the assumption is not justified. The phenomena of living organisms, and especially those of the higher forms, are so complex that it is impossible to make this assumption about them with the same degree of certainty. There is a strong presumption, however, that the phenomena of life and of psychology follow orderly sequences closely related to and intimately associated with the phenomena of material things.

Professor G. N. Lewis has recently pointed out, however, that in accordance with the principles of relativity and mathematically considered, we should speak of time as "two-way" rather than as unidirectional. He also says that from this point of view we have the same right to say that an event is caused by events in the future as that it is caused by events in the past. This does not change, in the slightest, the fundamental assumption of science, that we live in a universe whose parts are consistently interrelated and dependable.

II. Cosmogony

The first hypothesis about the world seems to have been that of a flat earth with a firmament above that "divided the waters which were under the firmament from the waters which were above the firmament." The sun, which seemed to pass over the heavens, was supposed to make its way back to the East around the outer circle of the flat earth. There is no evidence that any writer of the Hebrew or Christian Scriptures got beyond these primitive ideas.

In the second century of our era, the Ptolemaic hypothesis was developed. This was based on the idea of a spherical earth with the sun, moon and planets revolving in orbits of which the earth was the center. By this means and a system of "epicycles," it was possible to predict eclipses and other astronomical events with considerable precision.

In the sixteenth century, Copernicus gave the world his hypothesis of a solar system with the earth turning on its axis and revolving about the sun. With the principles of inertia and gravitation, Newton developed the hypothesis further and astronomical observations have made it possible to predict occurrences in the system with a marvelous degree of accuracy. Recently, the Michelson-Morley experiment, demonstrating that the apparent velocity of light is independent of the direction in which the observer and the earth on which he is working, move, has led Einstein to de-

velop new principles which have caused a slight modification of Newton's hypothesis. Very careful observations have given results which agree with Einstein's theory of relativity.

As we look back over this rough and superficial outline of the development of our knowledge of the relation of the earth to the other bodies of the celestial universe, it is evident that even the first, crude hypothesis of a flat earth and a firmament above, corresponded in some degree to the universe which better hypotheses and more accurate observations have revealed to us. The first ideas were not entirely false and we can have no certainty that the latest are entirely true. There can be no reasonable doubt, however, that these latest ideas correspond more closely to the realities about which we are endeavoring to gain a knowledge.

The hypotheses about cosmogony and the formation of the earth, found in Genesis, were not original with the Hebrews but were borrowed from the writings of earlier and more cultured peoples. No attempt was made at the time nor for several milleniums afterwards, to compare these hypotheses with the history of the earth found in the rocks. The hypothesis of a flat earth and a firmament above was founded on direct, though very superficial observations. The hypothesis of the formation of the earth by a creative fiat was so speculative and so totally unrelated to any facts known by its authors that it has been of no appreciable value in discovering the occurrences which took place during the geologic ages.

The nebular hypothesis of Hershel and Laplace was the first scientific hypothesis about the possible origin of the earth. It was suggested, in part, by the rings of Saturn, but its foundation on observation was very slender and so many facts inconsistent with the hypothesis have been discovered that it no longer deserves serious consideration.

In comparatively recent years, Chamberlin, Moulton and others have developed a quite different hypothesis to ac-

count for the origin of the solar system. They suppose that many hundreds of millions of years ago a large heavenly body came near enough to the sun to cause large masses to splash out and to be drawn away from the sun by the attraction of the other body. These masses were given sufficient velocity at an angle with the direction of the sun's motion to cause the materials to assume elliptical orbits about the sun. According to this "planetesimal hypothesis" the nucleus of the earth at first formed was comparatively small and it has received accretions, at first rapidly and then more slowly, until it finally acquired its present form and dimensions. This hypothesis has been worked out with very great care, taking into account facts and mathematical reasoning of the greatest variety and it rests on a very different basis from that of the nebular hypothesis. It is now favorably received by those who are most competent in this field.

Instead of a world which seemed large and all-important to the ancients, we now know that the earth is a mere speck in a universe reaching out millions of light years on every side. Our solar system is so isolated from other large bodies, however, that it has been speeding on at the rate of 12 miles a second, in relation to our galaxy, for several hundred million years since it came close to any body large enough seriously to affect its constitution.

Both the spectroscope, and the composition of meteors which fall from the sky, have demonstrated that throughout the vast universe all material substances are composed of the same chemical elements.

III. Geology

The period which has passed since the oldest sedimentary rocks were deposited beneath an ancient ocean is measured by the thickness of the strata, by the erosion through these strata of such rivers as the Colorado, and by the age of radioactive minerals. Even a layman who has seen the Colorado Canyon, can get some idea of the ages required to

deposit the materials forming the strata there exposed to view and then for the river to cut down and form a valley one mile in perpendicular depth.

It was formerly supposed that the interior of the earth is in a molten condition, but the experiments of Michelson and the calculations of Moulton have shown that, whatever may be the temperature of the interior, it is in a condition twice as rigid as steel. On the island of Hawaii there are two volcanic craters filled with molten lava at a difference of level of some thousands of feet. It is impossible that these two bodies of liquid are directly connected and it is highly improbable that the liquid lava of any volcano is anything else than a local phenomenon of very limited extent.

A determination of the density of the earth and also the rate of transmission of waves from earthquakes has demonstrated that the central portion is different in composition from the surface and probably consists largely of iron. The composition of meteorites gives some support for this opinion.

Determinations of the force of gravity by means of pendulum experiments and elaborate calculations made at the Coast and Geodetic Survey, in Washington, have very fully established the theory of isostacy. The crust of the earth is in a state of nearly stable equilibrium with high mountains above materials of low density and deep oceans above portions of the earth heavier than the average. The slow wearing down of the mountains by the action of the elements must disturb this equilibrium, however, and may have been an important factor in the tilting of strata and other cataclysmic phenomena for which there is abundant evidence.

Lord Kelvin's estimate of forty million years as the time required for the earth to cool from a molten condition to its present state, was completely discredited by the discovery of the wide dissemination of radioactive minerals, which continually evolve heat by their disintegration. The

much longer period claimed by geologists on the basis of the records in the rocks is more probable.

It seems evident that if we excluded from geology everything not fully and accurately known, there would be practically no science left. The most important part of geology is not an account of the facts which have been observed, but the interpretation and correlation of those facts into a systematic body of knowledge.

IV. Physics

The assumptions that there are two kinds of force which exert an attraction between bodies, gravitational and electrical, and also an electrical force exerting a repulsion, are among the most common concepts of physics. Galileo seems to have been the first to grasp fairly clear ideas about the relation between force and motion. The idea that a force acting continuously on a body will produce a continually accelerated motion must have been at the basis of his question of the view of Aristotle that a heavy body will fall faster than a light one. When he dropped a heavy and a light ball from the top of the leaning tower of Pisa and found that they came to the ground together, he struck a blow at authority from which it has never recovered. And when he demonstrated the laws of accelerated motion by using inclined planes, he illustrated the fact that ideas or hypotheses almost invariably precede useful experiments.

The proposals of the corpuscular theory of light by Newton and of the undulatory theory by Huyghens, occurred about two hundred and fifty years ago. The discoveries of the phenomena of interference, of light pressure, of the independence of the apparent velocity of light of the direction in which the observer is moving through space, and the wave motion of electrons as shown by interference phenomena have given some physicists the conviction that both theories give some approximation to realities not yet fully understood. The subject is in such a state of develop-

ment that it would be presumptuous for an outsider to express an opinion. The hypothesis of an ether seems to be rather definitely avoided. The rapid changes in this branch of physics seem to be a chief reason why many physicists question the possibility of gaining a knowledge of things which cannot be directly observed or measured.

The relations between the elastic properties of air under adiabatic expansion and contraction, the velocity of sound waves through the air, and the standing waves shown by lycopodium powder compared with the number of vibrations per second as shown by the counter of a siren, are accepted as a very complete demonstration that sound is propagated by a to and fro motion of particles of air in the direction in which the sound travels. No one has seen the particles of air move and it might be of interest for the scientific purist to inquire how much of his mental picture of sound waves is hypothesis and how much is actually observed fact.

Electrical phenomena of a simple kind were known to the ancients but they had no suspicion of the nature of lightning, and it is barely two centuries since it was discovered that some substances conduct electricity and others do not. A very few years later vitreous and resinous electricity were distinguished. About 1750, Franklin suggested that a body charged with vitreous electricity contained an excess, and one charged with resinous electricity a deficiency of the "electrical fluid." As the electrical charges with which he experimented were due to an excess or deficiency of electrons, his nomenclature was fully justified. Unfortunately, he made a bad guess as to which of the bodies contained an excess of the "electrical fluid." For this reason the language of books on physics and electrical engineering seems destined to be permanently confused.

Physicists had to wait till the very close of the nineteenth century for the discovery of the electron, an atom of negative electricity, and the determination of its electrical mass

in comparison with the electrical mass of a hydrogen atom. It was still later when the proton, the nucleus of a hydrogen atom, was recognized as an atom of positive electricity.

Without any satisfactory hypothesis about the nature of electricity, it was possible to define such terms as "potential," "current" and "resistance" in such a manner that they could be treated mathematically and a satisfactory system of quantitative measurements and of so-called "absolute" units built up. When it was discovered that the ratio between the units developed from electrostatic and those derived from electromagnetic attraction is the velocity of light, there could be no doubt about the intimate connection between electricity and light. Some years later, long electrical waves were discovered by Hertz and wireless telegraphy was developed. It is now generally accepted that the long waves of the radio, the long heat waves which bring a large part of the heat coming from the sun, the short waves that affect the retina, the very short x-rays, supposed to originate in the electrons close to the nucleus of every atom and the penetrating or "cosmic" rays discovered by Kolhörster, and supposed by Millikan to be generated when protons and electrons combine to form helium and other atoms, are all varieties of the same class of phenomena.

The fact that the science of electricity was developed for a long period with no satisfactory fundamental hypothesis may be one reason why some physicists are inclined to the view that we can gain no real knowledge about things which cannot be seen or measured. But the literature of physics for the last thirty years is full of hypotheses about electrons and the function they perform in the formation of spectral lines and in other phenomena. It was sixty years after Dalton proposed his hypothesis before chemists agreed on principles which enabled them to prepare a satisfactory table of atomic weights, and one hundred years before Ostwald admitted that the evidence for the existence of atoms can no longer be reasonably questioned. While we can never ex-

pect to observe either atoms or electrons directly, effects believed to be due to the action of single atoms and single electrons have been seen and few persons familiar with these facts doubt that electrons and atoms are real. We may reasonably hope that during the next forty or fifty years our knowledge of electrons will develop somewhat as the knowledge of atoms has developed during the last century and a quarter.

V. Chemistry

The term element was first used of earth, air, fire and water, not one of which is an element in the modern sense. Associated with these elements were four properties, cold, dry, hot and moist. Each element had two of these properties and each property was common to two elements.

Earth
Cold Dry
Water Fire
Moist Hot
Air

These elements still persisted in the literature of alchemy and chemistry till near the close of the eighteenth century.

For more than a thousand years men followed the idea that it was possible to discover a Philosopher's Stone which would transmute baser metals into silver and gold. Even Francis Bacon, at the time of Shakespeare, considered such a transmutation possible. Slowly, after centuries of futile search, men were convinced that the quest was useless. The demonstration that an idea is false is often an important but difficult step in the advance of science. The idea of transmutation was false for that time, although it has now been shown that transmutations occur.

The work of the alchemists was not useless, though it failed of its goal. During centuries of experimentation some useful knowledge was gained and the habit of experimenta-

tion was established and developed to a far higher degree than in any other branch of science.

The first important generalization in chemistry was the theory of phlogiston. This is often spoken of as false and at the time of Lavoisier it was completely abandoned. If we put "energy" in place of the word "phlogiston," however, we shall find that the theory was partly true.

The idea that matter is discontinuous came from the Greeks. It was held by Newton and others, as a philosophical speculation, with very little reference to facts in its support. Dalton got the idea from Newton and, very early in the nineteenth century, he added the idea that chemical action takes place, not between masses of substances, but between the atoms of which they are composed, that these atoms have definite weights and that the gravimetric composition of compounds furnishes a means of discovering the relative weights of the atoms.

There is, perhaps, no better illustration of the value of a hypothesis in gaining a knowledge of things which are beyond the realm of direct observation and experiment. Ten years before Dalton proposed the hypothesis that the smallest particles of chemical elements have definite weights, Richter in Germany determined with considerable accuracy the quantities of eight bases which combine with 1000 parts of sulfuric acid and the quantities of seven other acids which combine with these amounts of the bases. The relations are given in the following table:

Acids		Bases	
Hydrofluoric	427	Alumina	525
Carbonic	577	Magnesia	615
Muriatic	712	Ammonia	672
Oxalic	755	Lime	793
Phosphoric	979	Soda	859
Sulfuric	1000	Strontia	1329
Nitric	1405	Potash	1605
Acetic	1480	Baryta	2222

If the quantity of any base which combines with 1000 parts of sulfuric acid is determined, the table gives at once

the quantity of each of the other acids which combines with this quantity of that base. Richter had in his hands a far more accurate demonstration of the law of combining weights than Dalton ever had. Because Dalton grasped the idea of atoms of definite weights as the cause of the phenomena he observed, while Richter did not think of this explanation, Dalton's idea has been the most fundamental guiding principle in the development of chemistry and physics ever since, while Richter's work has been almost completely forgotten.

Dalton failed to find any means by which he could distinguish between combining weights and true atomic weights and he made a number of bad guesses about the latter. For fifty years chemists failed to come to any satisfactory agreement in choosing atomic weights and many of them said that it was impossible to select true weights and that the combining weights were all that was necessary for the development of chemistry. Such an attitude is closely parallel with the attitude of those physicists who say that we need not concern ourselves about the orbits of electrons because we have no observational method of learning about them.

Avogadro proposed his hypothesis that equal volumes of gases, under the same conditions, contain equal numbers of molecules, very soon after Dalton proposed the atomic hypothesis, but it was fifty years later when Cannizzaro presented the matter in such a convincing manner before a meeting of chemists in Germany that the chemists of the world accepted the hypothesis as a basis for the selection of atomic weights. The atomic weights selected are now so reinforced by the law of Dulong and Petit, the isomorphism of related compounds, the Periodic System of Mendeléef, the atomic numbers of Mosely and the atomic weights of isotopes determined by Thomson and Aston, that it is difficult for one familiar with these relations to doubt that we know the relative weights of atoms which no one has ever seen.

The theory of valence of Frankland and the theory of chains of atoms of Couper and Kekulé, combined with the earlier theories of radicals and substitution, have given a knowledge of the sequence in which atoms are attached to each other in 250,000 compounds of carbon.

By means of more recent hypotheses about the structure of atoms and the function of electrons in chemical combination, chemists and physicists are slowly feeling their way into other realms of the unseen. We can hardly believe that the methods which have been so successful in the investigation of molecular structures will fail in the new fields so recently entered.

In the middle of the nineteenth century, Bunsen the chemist, and Kirchhoff the physicist, established the relation between the dark, Fraunhofer lines of the solar spectrum and the bright lines produced when compounds of sodium or of other elements are excited in the Bunsen flame or by an electric spark. Kirchhoff demonstrated that an incandescent vapor absorbs light of the same wave-length which it emits. Assuming, therefore, that there is sodium vapor in the photosphere of the sun, that portion of the white light coming from below, which has the same period of vibration as the sodium atom, will be taken up by the vibrating atoms and the light which has been robbed of these vibrations will show dark lines in the spectroscope. This gave, at once, a means for determining the chemical constitution of the sun and stars and has immensely extended our knowledge of the universe in which we live.

VI. Electrons and Quanta

After the discovery of electrons and of the disintegration of radioactive atoms, after the proposal of Planck's hypothesis that energy of radiation is given out and absorbed in quanta, and after Rutherford had demonstrated that the mass of an atom is mostly concentrated in a very small nucleus having a positive charge, Bohr developed his hy-

pothesis that atoms consist of such nuclei surrounded by rotating electrons. He supposed that the speed of the rotation of an electron is dependent on its distance from the nucleus and the magnitude of the positive charge, very much as the speed of the rotation of the earth in its orbit is less than the speed of rotation of Venus because the earth is farther from the sun. Bohr made the further supposition that when one of these rotating electrons receives a quantum of radiation of the right period it may be lifted from its orbit to one further from the center. Such an electron may then fall back to its original orbit and give out a quantum of radiation of the same period as that absorbed.

By this hypothesis, Bohr furnished a more definite meaning for the vibrations which had long been accepted as the cause of the spectral lines. Since the proposal of the theory, new properties of electrons have been discovered and considerable modifications of the theory are in progress, but its success has been so great that we have good reason for thinking that it is a first, and very useful, approximation to the reality.

Some of the hypotheses about the relation between electrons and chemical combination will be presented in a later chapter. Enough has been said to make it clear that the ideas which have guided chemistry to its greatest successes were not dependent, primarily, especially in their inception, upon direct observation and mathematical reasoning but that they have been developed, and, as we think, brought to a closer approach to reality by a "cut and try" method.

VII. Life

The origin of life is shrouded in even greater mystery than the origin of the earth. If the earth was once in a molten condition, as seems almost certain, life must have originated on it at some time, but it has been impossible to discover any conditions which will produce new life. No suggestion as to how life may have begun has gone beyond

the stage of mere speculation. Seventy years ago Pasteur undertook a careful investigation of spontaneous generation. At the close of his studies he gave an address at the Sorbonne in which he said:

Consequently, gentlemen, I can say to you as I show you this liquid: I have taken from the immensity of creation a drop of water and have filled it with a fecund jelly, that is to say, in the language of science, full of the elements appropriate for the development of the lowest forms of life. I wait, I observe and I question it and demand of it that it shall recommence for me the primitive creation; that would have been such a beautiful spectacle! But it was dumb. It has been dumb for many years since these experiments were begun. Ah! How far was I then, how far am I still from the single thing which it has not been given men to produce—the germs which float in the air; how far from life, for life is the germ and germs are life. Spontaneous generation will never recover from the mortal wound which this simple experiment has given it.

This conclusion of Pasteur still holds. However, any chemist who remembers that thirty years ago all chemists would have agreed that a transmutation of the elements was impossible and recalls the discoveries of transmutations made since then, will be very modest in claiming that the conditions for spontaneous generation will never be discovered. All we are justified in saying is that the origin of life is, as yet, an unsolved mystery.

That living, organized matter is different from dead matter, cannot well be denied. The two most important characteristics of life seem to be the power of reproduction and the coordinating power by means of which the higher organisms, especially, conduct themselves as units, both in their physical development and in their psychological conduct. While the physical and chemical relations in living bodies are, so far as can be learned, exactly the same as in non-living matter, the two characteristics mentioned con-

stitute a line of demarcation which dead matter has never been known to pass.

The relations between living and dead matter are, however, much closer than the last statement may seem to indicate. The paleontological record furnishes conclusive evidence that living beings have progressed from lower to higher forms during long ages. Until the middle of the nineteenth century, it was generally believed that new forms appeared by special creation. After many years of study, Darwin became convinced that the various, so-called species, are genetically related and that the changes found in the paleontological record are due to the slow accumulation of slight differences. He thought that a process of "natural selection" caused forms not suited to their environment to perish in the struggle for existence.

The principle of natural selection is still considered an important factor in evolution but much importance is now attached to "mutations" which occur for reasons little understood. All biologists of standing now accept the hypothesis that the higher forms of life, including the human race, are genetically related to lower forms. Just as the atomic theory has been of constantly increasing importance to all branches of the physical sciences and to biology, the theory of evolution has caused a complete revolution in the attitude of men toward all branches of historical, social and political science as well as toward biology. Instead of a golden age behind us and a fall from a high estate, we are now justified in looking for the golden age in the future.

VIII. Heredity

Not long after the publication of Darwin's *Origin of Species*, an Austrian monk, named Mendel, discovered that in sexual reproduction, whether animal or vegetable, there are two sets of unit factors, called genes, one derived from the ovum and the other from the sperm cell. In the maturation of the sperm and of the ovum one-half of these unit

factors are eliminated, partly from the ovum and partly from the sperm, in accordance with laws of inheritance which are now well defined. Two classes of such genes are recognized, "dominant" and "recessive." Thus in guinea pigs (not in man) black is a dominant gene and white is recessive. Following the Mendelian laws, if a pure black guinea pig is mated with a pure white, all the offspring will be black. But if these black hybrids are interbred, they will produce, on the average, three black pigs and one white. If whites of the second generation are interbred or are bred with a pure white, there will be only white offspring. One of the black pigs of the second generation, if bred with a pure white, will produce only blacks. But if the other two black pigs of the second generation are crossed with pure whites, half of the offspring will be white and half black. The details have been carried much further and the average number of individuals showing dominant and recessive characters can be predicted. It is evident from Mendel's laws that certain genes are represented in the reproductive cells which are not apparent in the parent and which may or may not appear in the offspring and that while it is impossible to predict what will happen for some given individual of the next generation, the statistical averages may be accurately predicted.

More recently, a very satisfactory explanation of Mendel's laws has been found in the conduct of the chromosomes in the formation of the male and female germ cells and in the union of these cells to form a new individual. These studies have thrown a flood of light on the mechanism by which hereditary characters are transmitted from one generation to the next. They explain the diversity of offspring from the same two parents and have laid a foundation for the beginning of a scientific study of eugenics.

By a careful study of many generations of some of the lower organisms, it has been possible to show, with a good degree of probability, that certain genes reside together

within a single chromosome. Furthermore, in some cases individual chromosomes have distinctive characteristics which may be related to definite gene groups. There is evidence, also, that the genes within a chromosome are arranged in a definite, linear order. There is some resemblance between such evidence and the evidence by means of which chemists determine the structure of organic compounds. The phenomena of life are so complex, however, and these new methods of study are so recent, that the conclusions must be accepted with some reserve. These studies furnish an excellent illustration of the scientific method. Some one got the idea that, when two characteristics are frequently associated in offspring, the chromosomes carrying these characteristics are probably located close together in the germ cells. This idea has led to long-continued experiments and the results have rendered very probable the truth of an idea which it has not been possible to test by direct observation of the chromosomes.

IX. The Human Race

The discovery of the true history of the human race is an important branch of science. The earliest history is recorded only by a few skeletons, stone implements and weapons and a few pictures by early artists.

Four periods, during which large ice caps were formed covering northern Europe and America, have left very definite records. Probably between the second and third, and quite certainly between the third and fourth of these glacial periods, animals appeared in Europe whose skeletons show many of the characteristics of the human race and who fashioned crude stone implements. Whether this Neanderthal race was genetically connected with the human race of today is uncertain, but the general opinion of anthropologists seems to be that the Europeans of today are descended from another race, which probably came from the east. It will be necessary to wait for further accumulation of evi-

dence and better interpretation of the evidence now in hand, before settled conclusions can be reached. There is no reasonable doubt that animals closely resembling man have lived on earth for tens of thousands and very possibly for a hundred thousand years, or more. The character of the stone implements left by the men of prehistoric times shows that children copied the methods of their fathers with little change during thousands of years. There was, however, a slow advance.

X. History

From the beginning of written records, perhaps six or eight thousand years ago, progress has been immensely more rapid. It is evident that from that time onward the interaction of men and women on each other has been far more important than any changes in physical heredity. The advances have been intellectual rather than physical.

It is entirely possible and quite as necessary to apply the scientific method to the study of the race during the period of written history as during the stone age. The same methods used in biology, must be employed in selecting the facts pertinent to the purpose for which the history is written and in sifting records which are untrustworthy, incomplete or prejudiced. When written properly, history may as truly be called scientific as biology or any other branch of science.

XI. Psychology

The study of the human mind is even more complex and difficult than that of living bodies, though, in some sense, it is to be considered a branch of biology. Physically, the most important characteristic of man is the large cerebrum, which requires many years of training, for its development to full functional activity. If the training is of such a sort as to produce in the individual, what is called an "open mind," the response of the mind to an ever-changing environment continues throughout normal, healthful life.

The earliest method of studying the mind was by introspection, and this method led Aristotle to a very clear statement of the laws of memory. In comparatively recent times, introspection has been supplemented by a great variety of laboratory methods, which it is not necessary to recount. Quite recently a school of psychologists has grown up which claims to discard introspection and to rely wholly on the observation of the behavior of animals and men. Much new information of scientific value is being gained by this method but when we consider all the complicated characteristics of a well-trained brain it seems impossible to form an adequate picture of its conduct by observing the actions of other people without interpreting those actions, in part, by what goes on in our own brains.

It does not seem necessary for our purpose to discuss the application of the scientific method in sociology and political science. In spite of the complexity of the relations involved, a beginning of genuine scientific work has been made in these fields.

The function of philosophy is to integrate all branches of science and form from them a closely interrelated whole.

XII. Summary

We may summarize the function and the methods of science somewhat as follows:

It is the function of science to secure as complete a knowledge as possible of the universe in which we live and of which we are a part. It is impossible to draw any sharp line between portions of human knowledge to which the methods of science have been applied and other portions of knowledge which are, at present, beyond its scope.

We acquire our primary knowledge of the universe by observation, experiment and the testimony of others.

Long experience has given to scientific men the conviction that there is an orderly sequence of events throughout the universe, such that the same conditions are followed by

the same results. While this is a philosophical conclusion which, from its nature, can never be completely demonstrated, no exceptions have been established and it is tacitly assumed in all branches of science. A possible modification of the principle will be discussed further on.

Many portions of the universe about us are beyond the possibility of direct observation. We assume that the same orderly sequence holds for things which are unobservable and that we could understand the conduct of such things if we could see them.

To aid us in gaining a knowledge of things which cannot be observed directly, hypotheses are proposed. These are, of course, based on observation and experiment.

When no means is found for submitting the logical conclusions from such an hypothesis to further observation or experiment, the hypothesis remains dormant and almost wholly sterile, as was the case with the idea of atoms before the time of Dalton. When Dalton wrote, in 1808:

> In all chemical investigations, it has justly been considered an important object to ascertain the relative *weights* of the simples which constitute a compound. But unfortunately the enquiry has terminated here; whereas from the relative weights in the mass, the relative weights of the ultimate particles or atoms of the bodies might have been inferred, from which their number and weight in various other compounds would appear, in order to assist and to guide future investigations and to correct their results.

he added an idea from which it was possible to draw logical conclusions and from that time on it was possible to submit these conclusions to the test of agreement with experimental facts. At this stage it might well have been said of the atomic hypothesis, as J. J. Thomson once said of the theory of electrons:

> The theory is not an ultimate one; its object is physical rather than metaphysical. From the point of view of the physicist a theory of matter is a policy rather than a creed. Its object is to

connect or coordinate apparently diverse phenomena, and above all to suggest, stimulate and direct experiment. It ought to furnish a compass which, if followed, will lead the explorer further and further into unexplored regions. Whether these regions will be barren or fertile, experience alone will decide; but, at any rate, one who is guided in this way will travel onward in a definite direction and will not wander aimlessly to and fro.

When an hypothesis has been used in this manner for some time, several things may happen:

New facts may be discovered which cannot be satisfactorily explained by the hypothesis, or a better explanation of the facts may be found. Facts inconsistent with the hypothesis of phlogiston were slowly accumulated, and when Priestly discovered oxygen and Lavoisier explained its function in oxidation and combustion, the hypothesis was abandoned. The Copernican theory gives an explanation of the apparent motions of the sun, moon and planets, so much simpler and better than that of the Ptolemaic system that the latter was superseded. Truth is an agreement between our ideas and the realities about us and within us. Remembering this definition, we are prepared to see that the theory of phlogiston and the Ptolemaic hypothesis were not entirely false, that our knowledge of combustion is still very incomplete and that the Copernican system may not be entirely true.

Instead of the discovery of facts inconsistent with an hypothesis, new facts may be discovered which support it, and the hypothesis may be developed with a large amount of detail never suspected by its author. This is true of the atomic theory. The hypothesis has proved so successful that most chemists, at least, are convinced that many of our ideas about atoms are in close agreement with realities beyond the realm of direct observation. The evidence for the reality of atoms is certainly far better than much of the evidence on which we base our daily conduct. Our whole economic system is based on confidence in relations which are usually

trustworthy but which cannot be demonstrated as absolutely true.

Because of facts which seem to be inconsistent with an hypothesis, it may lie dormant or be abandoned for a time and later be revived and brought into general acceptance. Avogadro's law seemed to be inconsistent with the densities of phosphorus pentachloride and ammonium chloride. The demonstration of the dissociation of these compounds gave a satisfactory explanation of the difficulty and the development of the kinetic theory of gases and the use of van der Waal's constants have shown that when account is taken of the attraction between molecules near together, the law is of the same high degree of accuracy as Dalton's law of combining weights and Faraday's law of the relation between the amount of an electrolyte decomposed and the quantity of electricity passed through a solution.

Prout's hypothesis that atoms are formed by the condensation of hydrogen atoms was abandoned when it was demonstrated that many of the atomic weights are not exact multiples of the atomic weight of hydrogen. The discovery of isotopes has led to a revival of the hypothesis and to its general acceptance. Even the departure of the ratio between the atomic weights of hydrogen and oxygen from a whole number is now explained by the interconvertibility of mass and energy which has been demonstrated for electrons and is assumed for protons, the nuclei of hydrogen atoms.

Nearly all current scientific ideas are a combination of one or more hypotheses with observations and logical reasoning. As has been pointed out, the postulate that we live in a universe of orderly sequences is an hypothesis and it would be difficult to find any scientific idea which does not rest on that postulate. Some hypotheses, such as the atomic theory or the theory of evolution, have become very complex, including many diverse elements. Some of these elements are so well established that we have a right to hold

them with a very firm conviction. Even such theories, however, should not be held on the basis of authority, or the general agreement of those best qualified to understand the subject, but on the basis of a clear understanding of the relation of the theory to well-established observations and experiments. In all cases, the distinction between hypotheses and observed facts should be as sharply defined as possible, though it sometimes happens that a new hypothesis helps in the discovery of errors of observation.

Some of the most valuable laws of science are statistical in character. If we examine a thousand descendants from a pair consisting of one white and one black guinea pig, we can predict with considerable accuracy how many whites and how many blacks there will be among them, but it is impossible to predict whether the offspring of a particular pair will be white or black. The second law of thermodynamics depends on the observed fact that two bodies having a different temperature will, if in the neighborhood of each other, exchange their heat energies until they are of the same temperature. But if we imagine an invisible plane in a body of gas of a uniform temperature, no one would claim that the numbers and velocities of the molecules passing that plane in opposite directions at a given instant are absolutely identical. If they are not, for that instant, one part of the gas grows warmer and the other grows colder, contrary to the second law of thermodynamics. Still less is it possible to predict the course and velocity of a single molecule of a gas.

There seems to be some analogy between the uncertainties of heredity and of the path of a molecule of gas and the uncertainty of the conduct of a human being. Recently, on the basis of this analogy, an attempt has been made to escape from the doctrine that in a world of orderly sequences the conduct of an individual is predetermined by his heredity and environment. It is impossible to foresee whether Heisenberg's "principle of uncertainty" or some

other method will give a solution of the age-old problem of predetermination and free-will. We may be sure, however, that most of us will continue to hold the practical, common-sense doctrine that we are responsible for our conduct and that by deliberate choice we may influence our associates for good or ill.

The perspective gained by a study of the methods by which scientific knowledge has grown in the past should help us to avoid two extremes which are still rather current in the world: the attitude that science has gained such a complete knowledge of the underlying principles of the universe that the fundamental, rather materialistic ideas of the past will be the exclusive characteristic of the science of the future; or that, because our knowledge of the universe about us and within us is imperfect and must always remain so, we have not attained to any real knowledge of the character of that universe by the method of hypotheses, observation and experiment, and that we should return to the vagaries of mystical sources, such as revelation, innate ideas, Christian Science, theosophy and the like for the exclusive basis of our knowledge.

References

Lewis, G. N. "Two-way time." *Science,* 1930, **71**, 569.

Chamberlin, T. C. "Planetesimal hypothesis." *Astrophys. Jour.,* 1906, **22**, 165.

Chamberlin, T. C. *The origin of the earth.* Chicago: University of Chicago Press, 1916.

[redacted]

MOULTON, F. R. "Rigidity of the earth." *Astrophys. Jour.*, 1919, **50**, 346.

KOLHÖRSTER. "Penetrating radiations." *Physik. Ztschr.*, 1913, **14**, 1153; *Verhandlungen d. deut. physik. Gesellschaft*, 1914, **16**, 719.

MILLIKAN, R. A. "Cosmic rays." *Phys. Rev.*, 1926, **27**, 353.

MILLIKAN, R. A. "Atom building." *Science*, 1930, **71**, 640.

NEWMAN, H. H. Mendel's laws; Chromosomes, *The nature of the world and of man*. Pp. 388–403. Chicago: University of Chicago Press.

Chapter II

ATOMIC STRUCTURE

I. Introduction

Philosophical speculation concerning the structure of matter and the nature of material objects dates at least as far back as several centuries before Christ. Interest in these very general problems has waxed and waned periodically throughout the ages, but definite progress was not possible until the advent of exact scientific experimentation. The discovery of empirical laws governing the behavior of matter naturally led to attempts to fit these laws into a complete system based on a comprehensive theory of the structure of matter. Theories were at first designed to cover the easily observable phenomena such as the expansion of gases, freezing of liquids, and transfer of heat from hot bodies to cold ones, but during the past thirty or forty years a wide variety of so-called "subatomic phenomena" has been discovered which must be explicable by any general theory. The theories have, therefore, become more detailed and have been extended in some cases by the introduction of new postulates and in other cases by the rejection of useless and untenable parts with the substitution of new ones.

In the fourth decade of the twentieth century one scarcely feels called upon to justify scientific research, no matter how remote it may seem from anything apparently "practical." This is partly because it is becoming generally recognized that practical results are frequently just around the corner, even though hidden as yet from view, and partly because of a fundamental change in the attitudes of more and more people toward "knowledge." Even though the comforts of life are not increased even indirectly by some types of re-

search, it is recognized that an increase in our knowledge of the universe is a worthy object in itself.

It is true that research upon the structure and behavior of matter has led to "practical" results, and that periodically excitement has been aroused by the possibility of utilizing atomic energy, but more and more we are coming to realize the importance of the purely philosophical aspects of the problem. It is unfortunate, but seemingly unavoidable, that philosophical speculations cannot be confined to persons of real intelligence capable of utilizing at least the simplest of logic. Ideas on the structure of matter have been beset by many of the ills which beset ideas in theology, ethics, and social science. One could, if necessary, pursue this train of thought much further and find that the scientific world contains its own type of fundamentalist, its own crusaders, and its own gods whose authority is not questioned as often as it should be.

At the risk of opening ourselves to the types of criticism which we have just been levelling at others, let us pause for a few moments to consider some of the philosophical aspects of the problem we are about to discuss.

The publication of Darwin's *Origin of Species* probably marks the beginning of a revolution in the attitude of the average intelligent person of a civilized community toward the possibility of improvement. It is recognized that conditions may change or be changed and that improvement may result from a properly regulated environment. Reform movements, the attempt to prohibit things which are supposedly harmful, recognize tacitly the assumption that conditions need not be kept as they are. It is difficult for us to realize how fundamental a change in history this recognition has made.

Will the philosophy of modern theoretical physics lead to a revolution in thought comparable to that brought about by Darwin? The future only will answer this question, but it should be pointed out that we are now dealing with a very

abstract philosophy which it may be difficult for the average mind to grasp in its entirety. Much that we are to attempt to describe is the result of an abstract mathematical reasoning which seems, often, to be devoid of any contact with human experience.

Are we going to be satisfied, for example, with the knowledge that a falling object obeys certain laws which we could formulate very precisely after a careful experimental study, or are we going to proceed a step further and inquire why there is any gravitational force? And if we succeed in describing gravitational force in terms which sound very fundamental should we stop there? We might proceed on and on describing one phenomenon in terms of laws which may be derived from other concepts which in turn have their foundation still elsewhere. The problem which we are proposing here can receive, probably, no general answer. Some scientists would have us believe that we should endeavor to describe as wide a variety of phenomena as we can in terms of a theory based on the fewest possible *arbitrary* postulates. Since the correlation is to cover a large territory we must expect our theory to have the appearance of being very complex.

In the theoretical physics and chemistry of today the question as to the meaning of *reality* has become of paramount importance. To illustrate our meaning let us consider a box which is closed so that we may not examine its contents. We shake the box, we turn it over and we study it in all ways possible without opening it and we come to the conclusion that it contains a lead ball. Is the lead ball really there? Of course we cannot prove our point without opening the box, for the ball might be made of other materials or we might not even have a ball in the box but some other shaped object. But if, by assuming a lead ball is in the box, we are able to predict many of the properties in which we are interested and do not arrive at any conclusions contrary to our experience in dealing with the box, we are justified, in a

sense, in stating that the box *does* contain a lead ball. We may be wrong but as far as we are concerned the lead ball is a reality. We must not forget, however, that some bright person some day may show us how to open the box or how to examine its contents with x-rays and that our ideas concerning its contents may be proven to be wrong. In order to prove that we were wrong, however, it would be necessary to make use of some property of the box which we had not previously investigated.

Now the problem of atomic structure is very much like the problem of the closed box. We cannot see atoms, we cannot (except, perhaps, in one or two types of experiment) study even the effects of individual atoms. And yet atoms seem to us to be a reality, for by assuming that they exist we can correlate a variety of different phenomena. Moreover, by assigning definite properties to the atom we arrive at certain laws capable of experimental verification. The particular properties we have assigned to our atoms may not always fit and we may have to revise our ideas, but we may hope to arrive eventually at a set of properties which will be quite satisfactory. It is possible that some other set of properties would be equally satisfactory and we would have therefore at least two satisfactory theories of the structure of atoms.

From the above superficial discussion we see that we act in a certain sense as detectives who reconstruct a crime from circumstantial evidence. Many of the details of the reconstruction may be doubtful or even wrong, but, in some respects, that is immaterial if the right person is brought to justice.

In what follows concerning the structure of matter we shall endeavor to present experimental facts as clearly as possible and to indicate the broad outlines of the theories which are in vogue for tying together the information available. It must be kept in mind that the more recent theories are mathematical pictures which are difficult, if not im-

possible, to describe in terms of geometrical figures which can be visualized. The lack of a suitable geometrical model is a disadvantage from the standpoint of a popular presentation of the subject, but there are certain advantages to be gained by not confining ourselves too rigidly to a picture which we find it difficult to forget when it becomes advisable to do so. It is customary at the present time to keep certain pictures for a description (mostly qualitative) of certain phenomena and to realize that a general mathematical theory is necessary for a quantitative formulation of the behavior of atoms and molecules.

II. Early Ideas of Atoms and Molecules

Properly speaking, chemistry did not exist as an exact science until the latter part of the eighteenth century. It is true that the alchemists knew certain of the chemical elements and carried out experiments which were of some significance, but there were no broad guiding principles. The idea that a chemical element retains its essential characteristics in spite of the chemical and physical changes to which it is subjected became gradually one of the most fundamental and useful concepts of chemistry.

Ideas concerning atoms were slow in crystallizing. They are mentioned in the writings of the Greek philosophers, but since there was at that time no experimental science these ideas were largely unfounded speculation. The discovery of the law of definite and multiple proportions by Dalton led inevitably to the introduction of the atomic concept. Certainly the simplest "explanation" of this law involved the assumption of atoms.

No detailed structure of the atom was deemed necessary for many years. It is true that Prout (1815) had suggested that the atoms of all elements might be built up of atoms of the lightest element, hydrogen. This idea was discarded during the nineteenth century as the atomic weights of the elements were more and more accurately determined. Thus the

atomic weight of chlorine was found to be 35.19 times the atomic weight of hydrogen, the experimental error being much less than 0.19. We shall see later that Prout's hypothesis has been revived in a modified form and is now considered to be of quite fundamental importance.

Prior to the advent of Dalton's assumption of atoms, it had been recognized for nearly two centuries that many of the properties of matter could be explained by assuming atoms (more properly what we now call molecules) and studying their movements. Gassendi and Hooke in the seventeenth century proposed theories of this type, but much of the honor for the beginnings of the modern field of kinetics belongs to Bernoulli, early in the eighteenth century. Little definite progress was made at first, but it is recognized quite generally at the present time that many of the properties of gases, liquids, and solids may be accounted for by assuming that there are molecules and that they are capable of movement. Molecules could, as a first approximation, be assumed to be hard, indivisible balls whose collisions with each other obeyed the laws of mechanics.

During the nineteenth century Maxwell extended kinetic theory by introducing the concept that all molecules do not possess the same kinetic energy, but rather that some have high velocities and some low velocities, the vast majority having velocities not widely removed from the average. The law he deduced for the distribution of the molecules over the range of velocities is frequently called the Maxwell Distribution Law. With its aid kinetic theory has become one of the most useful tools of the physicist and chemist.

Thus we see that natural philosophers had arrived at the concept of molecules before they were deemed necessary to explain chemical phenomena. During the nineteenth century chemists were largely concerned with matters which did not require any discussion of the real nature of atoms. New compounds were made and the concept of valence, whereby atoms were joined together by definite bonds, per-

mitted the systematization of a large number of the facts of chemistry. Organic chemistry, in particular, underwent a striking development, for valence permitted an understanding of complicated molecules in which the application of the law of definite and multiple proportions was, at a first glance, not at all obvious.

III. Electricity and Radiation Before the Twentieth Century

In any discussion of the structure of matter we must inquire into the nature of electricity and of the manner in which electrical charges and matter are interrelated. Many electrical phenomena were known early in the nineteenth century. Volta, Ohm, Ampère, d'Arsonval and others had formulated laws governing the passage of electricity through conductors. To Faraday belongs, however, the honor of stating a law which is of fundamental importance for a discussion of the nature of matter. In Faraday's time many of the atomic weights were known as well as the formulae of many compounds. The atomicity of matter was, therefore, accepted by many scientists and Faraday's law introduced a concept leading to the atomicity of electricity. Faraday stated that if an electric current is passed through a conducting solution the amount of material formed at or dissolving from the electrodes bears a definite relation to the atomic weights. Thus a given amount of electricity (96,500 coulombs) will deposit one half a gram atom of copper or one gram atom of silver or one half a gram atom of nickel. Faraday's statement seems to imply that if matter is associated with electricity it can not be associated with any arbitrary amount but must take up a whole number of unit charges. Thus there would be two charges on a copper atom, one on a silver atom and two on a nickel atom. His announcement was made long before the electron had been introduced into physics and chemistry, but his law is seen to be a necessary consequence of the electron concept.

A discussion of recent developments in theoretical physics must be prefaced by a consideration of the nature of light (radiation). The science of optics had its origin in ancient history, for lenses and mirrors seem to have been used by the Assyrians and Egyptians. Geometrical optics received, however, its greatest impetus when the wave theory of radiation was introduced, presumably by Huygens about 1690. Light was then assumed to consist of a wave motion propagated in the ether, although the ether was merely introduced because waves moving in a perfect vacuum were inconceivable.

The wave theory did not explain entirely satisfactorily why light travels in straight lines and why it does not spread in all directions from a hole in a perforated shield placed in its path. Newton, therefore, introduced a corpuscular hypothesis which was temporarily adopted, but this was rejected in turn and the wave theory readopted following the experiments of Young and Fresnel on interference (early in the nineteenth century).

If two stones are thrown into a pond, waves will start out from each place where a stone encounters the water. When the two sets of waves meet there will be certain places on the surface where the crests of the waves of one set encounter and reinforce the crests of waves of the other set. At still other points the crests of one set will neutralize the troughs of waves from the other set. Thus one obtains some reinforcement of crests, some neutralization and some reinforcement of troughs. This is the phenomenon of interference and it has an analogue in the behavior of light waves, thus making necessary, apparently, the adoption of a wave theory.

The development of electromagnetic theory served to still more strongly intrench the wave theory. It was shown that the ratio of the electromagnetic unit of electricity to the electrostatic unit was equal to the velocity of light and furthermore that by treating light as electromagnetic waves

many different phenomena could be correlated and new ones predicted. Indeed the discovery of wireless waves by Hertz may have been the deciding factor in the adoption of the electromagnetic theory of radiation.

It is perhaps not too much to say that at the close of the nineteenth century physicists considered the nature of light to be completely understood. Since that time the corpuscular theory has been revived, but it is being realized more and more clearly that the electromagnetic wave theory may not be overthrown. We shall see how both concepts are useful, each as being the simplest way to consider certain phenomena.

This hasty summary indicates the state of affairs at the beginning of the last decade of the nineteenth century. A famous physicist stated during that period that little remained to be discovered and that research in physics would consist essentially in the refinement of measurements. A somewhat similar condition existed in chemistry.

IV. The Start of the Modern Era

In 1895, x-rays were discovered by the German physicist Röntgen and in 1896 radioactivity was discovered by Becquerel. These two discoveries may be said to have inaugurated research on the structure of matter of such scope that more developments have come in the last thirty years than in all previous history. And yet this development would have been impossible without what went before. One should be careful not to belittle our forebears, for their fundamental work in mathematics, physics and chemistry forms the basis for a great deal of modern science.

Prior to the advent of radioactivity, Sir William Crookes had shown that charged particles were produced in an evacuated tube containing two electrodes if a current from a spark coil was allowed to pass through the rarefied gas. It had been demonstrated that positive rays were produced which were relatively difficult to deflect by an electrical field

and that their nature seemed to vary from gas to gas. It was also known that negative rays were produced and that the nature of these rays seemed to be independent of the kind of gas. These rays possessed appreciable mass, for Sir William Crookes succeeded in causing a small paddle wheel to rotate when placed in their path.

It was soon discovered that radioactive substances give out three kinds of rays, one of which is attracted toward the negative pole in an electric field (now called alpha rays), the second of which is attracted toward the positive pole and seems to be similar to the negative rays observed in the evacuated tube. These are called beta rays. The third type of ray is not deflected by an electric field and seems to be very much like x-rays.

The alpha rays were shown by Sir Ernest Rutherford to give the gas, helium, when they were collected in a small glass vessel, so that we may think of them as atoms of helium with a positive charge. The beta rays, which are like the negative rays produced from all kinds of gases in the Crookes tube, are called electrons.

All matter, it seemed, consists of positive and negative electricity. How then are the positive particles and the negative particles put together to make atoms? This question has formed the basis for much speculation.

The first theory of much importance was due to Sir J. J. Thomson of Cambridge University. He postulated a sphere of positive electricity inside of which were placed the electrons. The electrons were thought of as small negatively charged particles. The theory did not receive general acceptance because it was not capable of precise mathematical analysis and because it seemed to disagree with certain facts connected with the Periodic System.

Rutherford is responsible for the first general statement of a theory which underlies nearly all subsequent detailed theories of atomic structure.

We may pause here to indicate the nature of the experi-

ments leading to this theory. Alpha particles are given out from radioactive substances with very high velocities, of the order of 1/10 to 1/20 of the speed of light or 15,000 to 30,000 kilometers per second. They have a positive charge of 2 (putting the charge on the electron as -1) and a mass of 4 on the atomic weight scale. When these rapidly moving charged atoms pass through matter they lose their kinetic energy, producing ionization and other effects in the molecules they encounter.

A rapidly moving alpha particle has the property of producing a tiny speck of light when it collides with a crystal of zinc sulfide. If such a crystal is placed below a microscope and subjected to alpha particle bombardment, it is possible to count by direct observation the number of particles hitting the crystal. Instruments of this type are called spinthariscopes.

The detailed study of the effects produced in matter by rapidly moving alpha particles has been of paramount importance in advancing our ideas of atomic structure. Particularly significant experiments were carried out in the laboratory of Sir Ernest Rutherford during the first decade of the twentieth century. Since alpha particles move with high velocities, they may penetrate quite large distances through gases and even through metals. In these experiments, alpha particles were directed at a thin metal foil. By placing the spinthariscope on the opposite side of the metal foil from the source of alpha particles, it is possible to determine the number which have passed through. By moving the spinthariscope around, it is possible also to ascertain the extent to which the particles are caused to deviate from their original direction. This study soon showed that some alpha particles suffered very large changes in direction in passing through the metal foil. In fact, it was shown that some were "reflected" and came back on the same side as that from which they came.

With Sir J. J. Thomson's theory of atomic structure, it

was possible to show that alpha particles would be little deflected on the average in passing through a metal foil and that the chance of "reflection" would be negligible. In view of these theoretical difficulties, Rutherford suggested that atoms consist of a small massive center with a positive charge (he treated it as a *point* in his calculations), now called the nucleus, and that the negative part of the atom is distributed in some manner in the surrounding space.

When the alpha particle, which is charged positively, approaches close to the nucleus of an atom, it will be repelled. In order for the particle to suffer a large change in direction, it must come very close to the nucleus and the latter must be very small so that the charge is located in a very small volume. Obviously, if atomic nuclei are considered as points and the alpha particle is considered also as a point, it would be possible to calculate nuclear charges from the average angle of deflection of the alpha particles. In this manner Rutherford was able to estimate the charges on the nuclei of certain heavy atoms such as platinum and gold. This charge, expressed in terms of the charge on the electron as -1, is now considered to be numerically equal to the *atomic number* (see the next few paragraphs). Thus the charge on the gold nucleus is $+79$ and that on platinum is $+78$.

This atomic model has formed the basis for most subsequent consideration. It remained for others to specify the distribution of the negative electricity in atoms.

V. The Atomic Number and the Nucleus

We have just seen that the charge on the nucleus of an atom is a characteristic quantity of fundamental importance. If an atom is to be electrically neutral, the amount of negative electricity surrounding the nucleus must be equal to the positive charge on the nucleus. What would seem more logical than to suppose that the lightest element has a charge of $+1$ on the nucleus, with one negative electron making up the rest of the atom, that the second element

has a nuclear charge of +2, etc.? By referring to the Periodic Table (Fig. 1) we see that hydrogen is the lightest element and we would assign to its nuclei, therefore, charges of +1. Helium nuclei would each possess charges of +2, lithium of +3, etc. However, if we arrange the atoms in their order of increasing atomic weight and number them in order, starting with 1 for hydrogen, we immediately get into some difficulties in the Periodic Classification of the elements (See Chapter III). In the Periodic Table, an alkali metal (lithium, sodium, potassium, rubidium and cesium) always follows an inert gas (helium, neon, argon, krypton, xenon and radon). Therefore, the nuclear charge of an alkali metal is always greater by one than the nuclear charge of the preceding rare gas and, moreover, the metal must have one more extra-nuclear electron. The atomic weight of potassium is, however, 39.1 and that of argon is 39.9. We must take liberties with our series based on atomic weights in order to get these two elements into their proper places in the Periodic System. In addition, are we sure that all of the elements have been discovered? If they have not our numbering would be erroneous.

It became essential to find some other method of determining the atomic number. One characteristic of an element is its x-ray spectrum, each element emitting, under proper conditions, waves of definite length. Moseley, in England, discovered that the heavier the element the shorter the wave-length of its characteristic x-rays. In fact careful investigation showed that the important quantity for determining the wave-length is the atomic number. A study of x-ray spectra placed the elements in their proper positions in the periodic system and permitted, moreover, a determination of the places for elements which remained to be discovered. The confidence in this method is so great that the determination of an x-ray wave-length is considered sufficient proof for the existence of a new element. Thus the element illinium, discovered by Hopkins and his co-

contain two types of atoms of weight 35 and 37 respectively. A third, of atomic weight 39, may also exist.

Prout's hypothesis may be modified to state that all atomic weights are nearly whole numbers, but not exact multiples of the atomic weight of hydrogen. The atomic weight of hydrogen is 1.008 and that of oxygen is 16.000, so that the difference between 16×1.008 and 16.000 is about eight-tenths per cent. If the hypothesis that all atoms are built out of hydrogen atoms is accepted, what has become of the excess weight? There has been much speculation upon this point. The theory of relativity of Einstein permits a calculation of the amount of energy which would be liberated if four atoms of hydrogen condensed to give one atom of helium of atomic weight 4.00. This amount is extremely large. It has been suggested that this process of condensation is taking place in the sun and in other hot stars and furnishes part of the energy which is lost by radiation.

If we assume that all atoms are built of hydrogen atoms and that the excess weight has been dissipated as energy, we may state certain facts connected with the nucleus. Since hydrogen (with the weight lost) has a mass of 1.000 and a charge of $+1$, an atom of calcium which has a mass of 40 and a charge on the nucleus of 20 must also have some electrons in the nucleus. The number of electrons in the nucleus would be given by the atomic weight minus the atomic number. Very interesting generalizations can be made from the atomic number, the atomic weight and the number of electrons on the nucleus. These need not be given in detail, but we may say in passing that nature seems to favor the even numbers as against the odd. Fig. 2 shows the relative abundance of some of the elements on the earth as a function of their atomic number.

It is convenient to mention here the subject of radioactivity (See also Chapter VI). Perhaps no other field of modern physical science has been so satisfactorily described in terms of a few simple postulates.

We have found already that radioactive substances emit three types of rays, namely alpha particles (helium nuclei), beta particles (electrons) and gamma rays (short wave-length x-rays). The alpha particle has a mass of four on the atomic weight scale and a charge of +2. Beta particles have

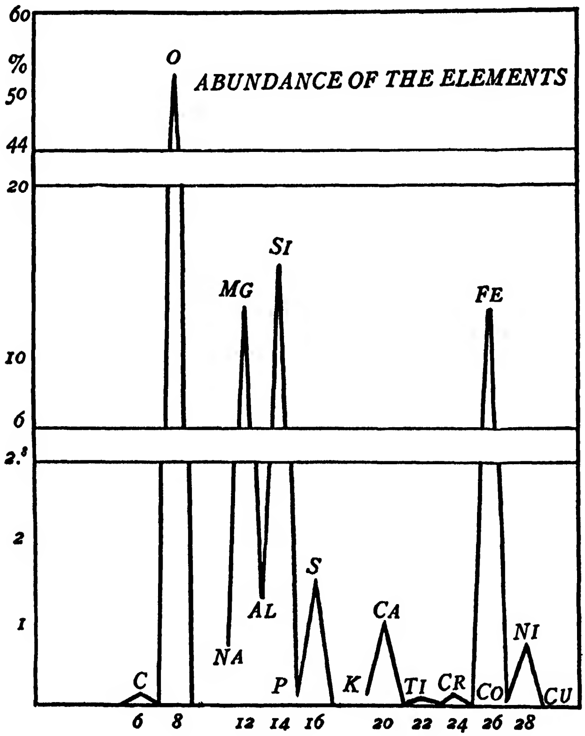


FIG. 2. Plot of the abundance of the element against the atomic numbers. By W. D. Harkins.

a very small mass, 1/1800 on the atomic weight scale and a charge of −1. Gamma rays do not possess a charge, but by the theory of relativity their emission may result in a de-crease in mass of the atoms from which they come.

The correlation of radioactivity data involves, among other things, the assumption that radioactive changes are

concerned with nuclear transformations. Uranium, for example, has an atomic weight of 238 and an atomic number of 92. If the nucleus of a uranium atom loses an alpha particle the remainder should have a mass of 234 and an atomic number of 90. By referring to the Periodic Table one finds that thorium has an atomic number of 90 and an atomic weight of 232. The disintegration of uranium has produced an atom having the same nuclear charge as an atom of thorium but differing from it in mass. We say that the new atom (uranium X_1) is an *isotope* of thorium.

If the new atom loses an electron from the nucleus, the atomic weight will not change but the atomic number will increase by one, for the removal of a negative charge has the same net effect on the total charge as the addition of a positive one. We would now have an atom of mass 234 and charge 91. Removal of a second electron (beta particle) would produce an atom of mass 234 and nuclear charge 92. Uranium has an atomic number of 92, so that our succession of three disintegrations (removal of one alpha particle and two beta particles) has produced an isotope of uranium.

There are three radioactive series, one starting from uranium as the parent element, another from thorium and the third of somewhat uncertain origin, although it was thought formerly to be a side branch of the uranium series. All of the radioactive series seem to give lead as the end product. Since the decrease in weight as we proceed down a radioactive series is due to the loss of alpha particles, the atomic weight of the lead produced in the uranium family must be given by the formula:

$$\text{Atomic Weight} = 238 - n\ 4,$$

and that for the thorium family by:

$$\text{Atomic Weight} = 232 - m\ 4.$$

If we put n equal to 8 and m equal to 6 we find 206 and 208 for the atomic weights of uranium lead and thorium lead respectively. The atomic weight of ordinary lead is 207.2, although samples of lead found in some uranium minerals

have been shown to have atomic weights very close to 206. Aston has shown by an independent method that lead consists of three isotopes of atomic weights 206, 207, and 208. Two of the three have just been accounted for as belonging to the uranium and thorium families. The remaining one of atomic weight 207 seems probably to belong to the actinium series, although there are several matters concerning this series which remain to be elucidated.

VI. The Planetary Electrons

The nucleus undoubtedly has a structure capable of mathematical analysis, but the attention of scientists has been focused primarily on the planetary or extra-nuclear electrons. Their number is equal numerically to the atomic number, so that the latter determines actually the characteristics of an element. The motions and configurations of these planetary electrons are directly responsible for the phenomena associated with x-rays, magnetism, spectroscopy and chemistry.

As we have already stated, Rutherford did not specify the positions of these electrons in his work on the scattering of alpha particles, merely postulating a positive nucleus of small dimensions surrounded by a diffuse cloud of negative electricity. Before we take up recent theories as to the distribution and motion of the planetary electrons, we must pause to consider briefly the nature of light or, more properly, of electromagnetic radiation. During the latter part of the nineteenth century, the wave theory seemed to be firmly intrenched. There was, however, one very perplexing problem which had not been satisfactorily solved. This had to do with so-called *Black Body Radiation.*

In any space at a temperature greater than the absolute zero (−273.2°C.), radiation is present. At ordinary temperatures, a very large fraction of this radiation is invisible to the naked eye and lies in the region of long wave-lengths, or the infra-red. An object which is heated begins to glow a

dull red at temperatures of a few hundred degrees and, when temperatures much over a thousand are reached, it is said to be white-hot. A vessel, which is entirely closed except for a small opening, will emit through this opening radiation whose characteristics depend on the temperature of the vessel. This radiation covers a large range of wave-lengths and is called *Black Body Radiation.* The distribution of the intensity among the various wave-lengths was quite accurately known from experiment, but attempts to derive a theoretical equation had failed. These efforts had been based on various assumptions, some in accord with so-called classical electromagnetic theory and some greatly at variance with these ideas.

In 1900 a German physicist, Max Planck, announced the derivation of a formula which gave satisfactorily the distribution of energy among the various wave-lengths in black body radiation. He made the radical assumption that an oscillator (which may be imagined as a molecule in the walls of the vessel) is not capable of possessing any arbitrary amount of energy, but must possess only a whole number of units of energy, called *quanta.*

In speaking of atoms we deal with particles of positive and negative electricity. The electron has a charge which, as far as we know, does not vary. The quantum, however, cannot be defined in such general terms, for its magnitude is found to be proportional to the frequency of the electromagnetic radiation emitted by the oscillator. There are, presumably, quanta of all kinds from the very large ones associated with x-rays and gamma-rays to the small ones associated with infra-red radiation.

The classical formula for black body radiation was known to agree with the facts reasonably well for the region of very long wave-lengths (infra-red). This formula involved the cube of the frequency. In Planck's derivation a formula was obtained which involved the product of the square of the frequency with the energy of one quantum. In order to

make the formula agree in every part of the spectrum, it was necessary to assume that the energy of a quantum is itself proportional to the frequency.

The frequency of a wave motion is equal to its speed divided by its wave-length. Hence infra-red waves, which may be said to have wave-lengths varying from a relatively large fraction of a centimeter, say 1/1000, down to 0.00007 of a centimeter (7000 Ångstrom Units, where one Ångstrom Unit is 0.00000001 or 10^{-8} centimeter) have frequencies from 30,000,000,000/0.001 = 30,000,000,000,000 (3×10^{13}) to 30,000,000,000/0.00007 = 429,000,000,000,000 (4.29×10^{14}), since the speed of light is 3×10^{10} centimeters per second. Visible light extends from about 7000 to 4000 Ångstrom Units with frequencies from 4.29×10^{14} to 7.5×10^{14}. The ultraviolet begins at this point and extends to higher frequencies, merging into the x-ray region. Gamma rays lie beyond the x-ray region. X-rays have frequencies of the order of magnitude of 3×10^{15} and gamma rays a hundred fold higher.

If the energy of a quantum is equal to a constant (Planck's constant $= 6.5 \times 10^{-27}$ erg seconds) multiplied by the frequency, it is readily seen that quanta in the infra-red possess the smallest energy of those mentioned and quanta of gamma rays the greatest energy.

Planck did not specify with great precision how the quantum concept was to be reconciled with the wave theory of radiation. The problem seems to have been left for the future, the only assumption necessary being that matter could only absorb or emit radiation by quanta. It was recognized still that the wave theory was entirely adequate for many purposes. Certain facts were already known and others were soon discovered which could be most simply explained by a somewhat extreme form of quantum theory, the wave nature of radiation being ignored almost completely. Thus it was known that electrons could be ejected from metals by the action of radiation. On the basis of the

electromagnetic theory this fact was not at all surprising, for radiation was considered to involve the propagation through space of two force fields at right angles to each other, one electric and the other magnetic. It was difficult to understand why the intensity of the radiation should not influence at all the speed of the ejected electrons. On the other hand the number was found to be proportional to the intensity.

To elucidate the difficulty in understanding the photoelectric effect we may make use of a crude analogy. Imagine a number of corks floating on the surface of a pond. Let a stone be thrown into the water, causing waves to spread out over the surface. We all know what will happen, namely that the corks will bob up and down as the waves go by. But in the photoelectric effect we do not get anything like this at all. We are quite surprised to find all but one of our corks to be totally unaffected by the waves, the one exceptional cork being thrown violently out of the water with a kinetic energy approximately equal to that of the stone when it encountered the water. The more stones we throw in the water the more corks will be ejected, but in each case the majority will be unaffected.

The problem becomes still more difficult when we realize that a cork several miles away will be ejected just as violently as one close by, the only difference being that the chance of ejection grows less as the distance grows greater.

Einstein proceeded to solve this difficulty by using the quantum theory in a form which approached the older corpuscular theory of radiation. Thus from a light source quanta are being shot out like machine gun bullets. An electron may be hit by and absorb the energy of a quantum, thereby being ejected from the metal with an energy equal to the energy of the quantum less the work done in removing it from the surface. Since half quanta are not supposed to exist, the electron either absorbs all of the energy or none of it. Just as there is less chance of being hit by random

machine gun fire at a great distance than at a small one, so the chance of ejecting a given electron will grow smaller as the intensity of the light grows less.

This theory of the photoelectric effect is now supplanted by one much more complete, but it was quite striking at the time it was proposed. Thus we see that the energy of ejection of the electrons should be proportional to the energy of the incident quantum, this in turn being proportional to the frequency. The constant of proportionality should be the same constant as that found by Planck in the formula for black body radiation. The excellent agreement between the values of this constant as determined by the two methods lent strong support to the theory. In fact Millikan and others have used the photoelectric effect to obtain one of the most accurate values of Planck's constant.

VII. Bohr's Quantum Picture

It is but a step from the Einstein theory of the photoelectric effect to the Bohr picture of atomic structure. We assumed in the above paragraphs that the electron in the metal either was unaffected by the radiation or absorbed an entire quantum, thereby being ejected from the surface. Bohr assumed that an electron in an atom either is unaffected by radiation or else absorbs an entire quantum, being ejected from the atom or changing from one position to another. In the photoelectric effect the kinetic energy of the ejected electron was equal to the energy of the absorbed quantum less the energy required to just get the electron out of the surface. In the Bohr atom, therefore, if a quantum is absorbed the energy is increased by an amount equal to the energy of the quantum. If a quantum is emitted the energy decreases by a like amount. This may be stated by a very simple equation. Let E_1 be the energy of some state of our atom and let E_2 be the energy of some other state. If a quantum is absorbed we may write

$$E_2 - E_1 = \text{energy of absorbed quantum} = h\nu \qquad (1)$$

close together that a very good spectrograph is necessary to make the spectrum appear really discontinuous. In addition there are periodic changes in intensity so that the spectrum has usually a fluted structure. A *band* begins at a definite place called the *head*, which may be either on the long or short wave-length end, and the intensity appears to fall off gradually as one proceeds toward short or long wave-lengths as the case may be. There is no definite place at which the intensity becomes zero, in some cases the end of one band even overlapping the head of another band. The spacing between the band heads follows usually a pronounced regularity. Band spectra are ascribed to molecules containing at least two atoms.

A third type, the continuous spectrum, is sometimes encountered. In this case no discontinuities are revealed even with the aid of a very good spectrograph. We need not consider this type further at this point.

Empirical formulae connecting the wave-lengths of the lines in the line spectra of various elements were known long before the invention of the quantum theory. With the advent of the quantum theory a connection between energy change in an atom and frequency of spectral line was established (Equation 1 above). Since the lines are very sharp in most instances, it seems necessary to conclude that the energy differences $(E_2 - E_1)$ may not assume any arbitrary values but will be limited to as many values as there are lines possible in the spectrum. From this one concludes that E_1, E_2, etc., *the energy states*, of the atoms, are very definite and that any given atom may exist in any one of a series of states, but that there is not a perfectly gradual change possible in the energy. The problem is to calculate the energy values, E_1, E_2, etc.

Bohr was the first to arrive at a quantitative expression for the possible energy values for the hydrogen atom. The mathematical difficulties were too great to permit the energy values for atoms containing more than one electron to

be calculated. For hydrogen the Bohr atom accepts as a starting point the Rutherford atom with a minute, heavy nucleus surrounded by negative electricity. The electron is treated as a point which revolves around the nucleus either in a circular or elliptical path. There will be an attraction between the positive nucleus and the negative electron so that the two may be prevented from coming together only by allowing the centrifugal force to counterbalance the attractive force. As long as this is done, classical ideas would permit the magnitude of the orbit to assume any possible value. The introduction of quantum ideas changes this aspect of the problem.

The frequencies of the first three lines of one of the principal series of hydrogen (Lyman series) are, in round numbers, 2.5×10^{15}, 2.9×10^{15} and 3.1×10^{15} respectively. Since energy differences are proportional to frequency, $E_1 - E_2$ will be less than $E_1 - E_3$ and this in turn will be less than $E_1 - E_4$, assuming that each line involves the transition from E_2, E_3 or E_4 to E_1. It is clear, therefore, that the possible energy values for the hydrogen atom are not multiples of any single quantity. It seems necessary to quantize something else than energy. Bohr limited the number of orbits by quantizing the angular momentum. For a circular orbit the product of the circumference of the circle by the momentum (mass times velocity) of the electron is assumed to be a multiple of Planck's constant. In other words

$$\text{Circumference} \times \text{mass} \times \text{velocity} = nh \qquad (2)$$

where n is a whole number. This assumption rigidly restricts the number of energy states for the hydrogen atom. The energies of the various states may be calculated by combining equation (2) with a few simple relations depending on the attraction between the electron and the nucleus as a function of the distance between them.

The formula derived by Bohr involves no *arbitrary* constants. The charge on the electron, Planck's constant, the

mass of the electron and the ratio of the circumference to the diameter of a circle are the only quantities other than n appearing in the equation.

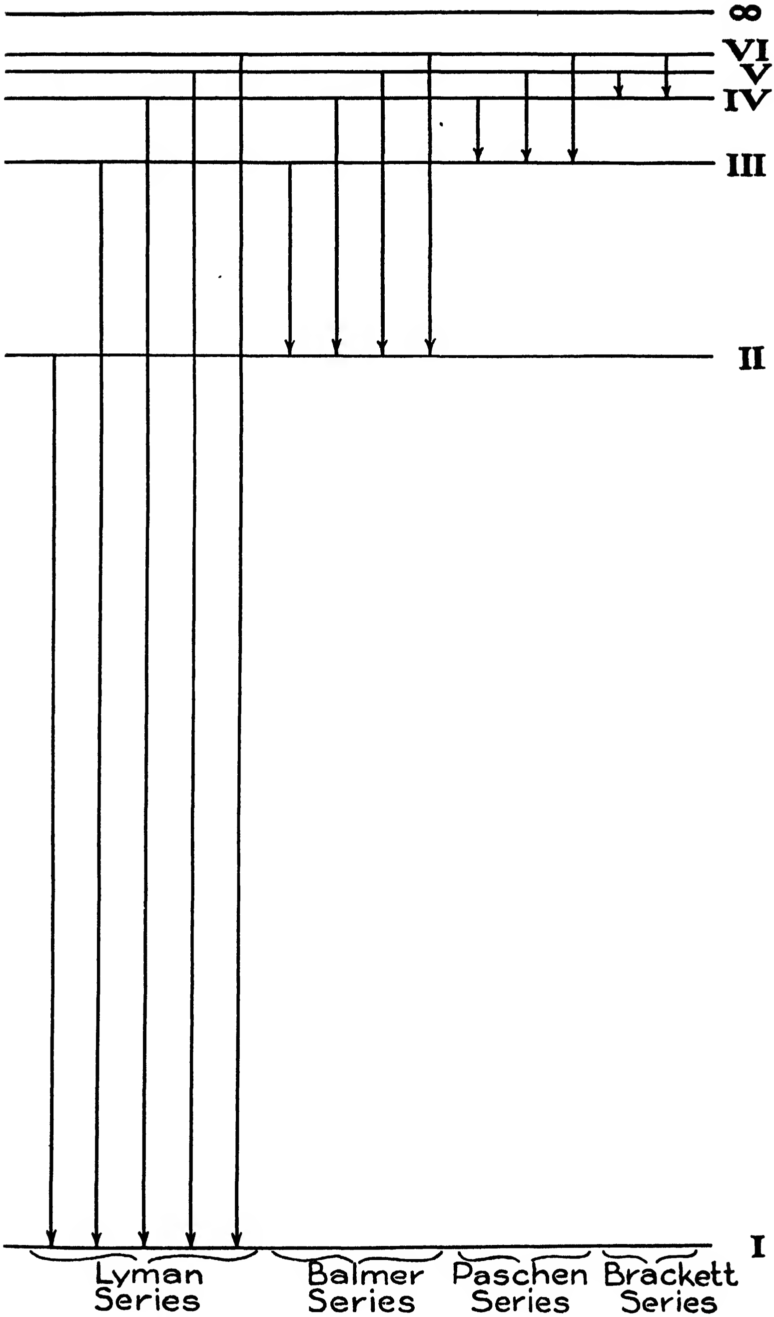
The characteristics of a circle are completely described by stating the radius. For an ellipse, however, two quantities must be specified, the major and minor axes, in order to determine its shape. For elliptical orbits two quantum numbers are necessary to determine the energy. The calculations in this case are much more complicated than for circular orbits, but the result shows that the energy of an elliptical orbit is *nearly* the same as that of a circular orbit having its diameter equal to the major axis of the ellipse. In fact the energies would be identical without the introduction of the theory of relativity which tells us that the apparent mass of the electron will vary with its speed. Thus we shall have several energy states with almost but not quite identical values. The number of such states will be determined by n in equation (2), for the sum of the two quantum numbers for an elliptical orbit will be equal to the value of n for the corresponding circular orbit. Thus if n is 3, we may obtain four pairs of whole numbers (3,0), (2,1), (1,2) and (0,3) each one of which adds up to three. One of the pairs involving a zero will correspond to a circle and the other to a straight line drawn through the nucleus. The latter type of orbit was deemed by Bohr to be physically impossible and was, therefore, excluded. This leaves us with three possibilities. It is easy to see that with a given value of n there will be n different orbits. The introduction of elliptical as well as circular orbits accounted for the fact that some spectral lines show a fine structure, that is that they really consist of a group of lines very close together. We will neglect for the moment this type of fine structure and discuss the broad characteristics of the spectrum of hydrogen atoms.

According to Bohr's theory there should be several series of lines in the spectrum of hydrogen. We will assume for the moment that circles and ellipses having the same quantum

number n possess the same energy. Then if an atom in state I absorbs energy it may be transferred to II, III, IV, etc. When the atom returns from a state of high number to one of low number, energy is emitted as radiation. If, however, the atom is already in state II, it may absorb energy and change to states III, IV, V, etc. Thus we shall have several series, the first having state I as the starting point in absorption and the end point in emission, the second being based on state II, etc. These relationships are shown in the accompanying diagram wherein each horizontal line represents a stationary state. The energy difference between any two states is proportional to the length of the vertical line joining them.

An interesting relationship is at once evident from the diagram. For example, if the energy change in passing from state III to state I is known and that involved in changing from II to I is substracted from it, the difference will be the energy involved in the III to II transition. Since, in the quantum hypothesis, energy is proportional to frequency, the frequency of the first line in the Balmer series is equal to the difference in frequency between the first and second lines of the Lyman series.

Additional evidence in favor of the idea of stationary states is obtained from ionization and resonance potentials. A heated metal will emit electrons. If the heated metal is in the form of a filament and is placed in a tube containing gas at low pressure, the electrons may be pulled away and given any desired kinetic energy by allowing them to be attracted by a metal plate which is positively charged. If there were no stationary states the electrons could lose energy to any atom they encounter. The quantum theory obviously prohibits this. As the charge on the plate is gradually increased, the electrons will eventually acquire sufficient energy to cause the electrons in hydrogen atoms they encounter to jump from state I to state II. The potential difference through which the electron must fall in order to


∞
VI
V
IV
III
II
I
Lyman Series
Balmer Series
Paschen Series
Brackett Series

accomplish this purpose is called the resonance potential. Obviously there will be as many resonance potentials as there are states to which the atom in question may be transformed. If the electrons acquire sufficient energy to cause complete removal of the electron from an atom they encounter, thus producing a positive ion, the potential through which they have passed is called the ionization potential. Quantum Theory permits us to equate the kinetic energy of the electron to the energy of the quantum emitted when the atom returns to its normal state. Excellent agreement between theory and experiment has been obtained in cases which have been investigated with care.

We have already mentioned that two quantum numbers are necessary to describe an elliptical orbit. By using both ellipses and circles a qualitative prediction of the fine structure of spectral lines was obtained. The application of the Bohr theory to elements whose atoms contain more than one planetary electron encountered insurmountable difficulties both from a mathematical standpoint and because theory did not agree with fact in such cases as could be treated approximately. It was soon recognized, however, that more than two quantum numbers are necessary to account for all of the observed facts. In addition to the two quantum numbers which determine the shape of the ellipse, a third was introduced which was supposed to correspond to the spin of the electron on its own center of gravity. A fourth quantum number was obtained by combining the spin quantum number with one of the two (orbital angular momentum quantum number) which govern the shape of the ellipse. Still other quantum numbers were necessary when the atoms were introduced into magnetic and electrostatic fields. Finally it became necessary to introduce a quantum number for the spin of the nucleus. This large assortment of quantum numbers causes the original simplicity of the Bohr atom to disappear completely and one is justi-

fied in asking whether it is useful to keep the original picture in mind at all.

As we shall see, the new and more successful theories of atomic structure involve a certain amount of abstract reasoning and they do not lend themselves easily to pictorial representation. It is recognized that the new theories are preferable to the old because certain difficulties in logic are removed and because results calculated with their aid agree with experiment better than those calculated from the Bohr theory. There is in existence, however, an enormous amount of spectroscopic information which must be tabulated and classified. The new theory does not lend itself readily to this type of systematic study. It has been demonstrated that this spectroscopic information may be classified and tabulated most conveniently with the aid of the quantum numbers touched upon in the preceding paragraph. It is true that the new theories involve whole numbers which correspond to the quantum numbers of Bohr in many cases, but we are no longer justified strictly in referring to orbital angular momentum, electron spin, nuclear spin, etc. We keep these terms merely because they are convenient for designating sets of numbers which are of use. By using these numbers we arrive almost invariably at the correct number of energy states and can describe many of the properties of atoms.

VIII. The Vector Atom

In classifying and tabulating spectra, therefore, we make use of several quantum numbers. Many of these quantum numbers are treated as vectors, that is quantities possessing direction as well as magnitude, and they may be added, subtracted and multiplied according to the rules of vector analysis. In this way a species of hybrid atom, frequently referred to as the vector atom, has been pieced together. It involves a curious mixture of the terminology of the Bohr

theory and the ideas of the newer forms of Quantum Mechanics, but it is of great use to the physicist and to the chemist.

Incorporated in the vector atom is one principle which we have not stated heretofore in this chapter. The *Pauli Exclusion Principle* states that no two electrons in a given atom may have completely identical sets of quantum numbers. With the aid of this principle the vector atom accounts remarkably well for the placing of elements in the periodic system. Its introduction was justified largely by the results to which it led, but it is shown to be of quite fundamental importance. The Exclusion Principle may also be derived by the more abstract methods of reasoning of the new mechanics.

Let us examine a few simple relationships brought out clearly by a study of spectra. The elements of atomic numbers 1 to 8 in order are hydrogen, helium, lithium, beryllium, boron, carbon, nitrogen and oxygen. Hydrogen atoms each possess one planetary electron, helium two, lithium three, etc., to oxygen with eight. If one electron is removed from an atom there will be left the same number of electrons as an atom of the preceding element in the list will possess. Thus removal of one electron from an oxygen atom will leave seven electrons which is the number attached to a normal nitrogen atom. If seven electrons are removed from an oxygen atom, only one will remain and we should have a "stripped" atom which is like the hydrogen atom with the one difference that it has a nuclear charge of eight instead of a nuclear charge of one. There should, however, be definite similarities in the spectra of hydrogen and of oxygen minus seven electrons. Similarly, singly ionized beryllium should have a spectrum like that of lithium, but differing in wave-length. These interesting relationships are predictable from theoretical considerations and are amply verified by experiment.

An additional fact concerning the multiplicity of spectral

lines is accounted for satisfactorily by the vector model of the atom. Many, in fact, most, spectral lines consist of a group of lines relatively close together. It has been shown that elements of even atomic number give lines with an odd multiplicity, that is the line is single (singlet) or consists of three components (triplets) or five components (quintuplets), etc., whereas elements of odd atomic number give lines with an even multiplicity (doublets, quartets, etc.). The multiplicity of the energy states may be ascribed to the vector addition (quantized) of the angular momentum vector and the vector corresponding to the electron spin. Let us consider an atom with one valence electron possessing one unit of orbital angular momentum. The electron is supposed always to have 1/2 unit of spin. (The unit is always $h/2\pi$.) We may now add 1/2 and 1 vectorially, keeping in mind that the answer must be quantized. The values of the sum are either 1 1/2 or 1/2. Thus we will have two different states with the same orbital angular momentum and the same electron spin but different interactions between these quantities. The spectrum of this type of atom will consist of doublets, certain definite rules governing the possible transitions in these various quantum numbers.

Next let us consider an atom with two valence electrons such as mercury or the alkaline earths. Here we add the spins for the two electrons together vectorially giving us either 0 or 1. If the net spin is 0, the vector sum of the electron spin and the orbital angular momentum will always be the same as the value of the orbital angular momentum and we will have singlet states. If the net spin is 1, the situation is different. If the atom contains 1 unit of orbital angular momentum, the vector sum of 1 and 1 may be either 2 or 1 or 0, thus giving us three states usually not differing greatly in energy.

In addition to the fine structure of spectral lines described in the preceding paragraph, there is a so-called hyperfine structure of such a character that the lines may be resolved

only by very special means. Here the introduction of the nuclear spin as a vector quantity becomes necessary in the interpretation of the results. We do not wish to go into this matter in detail, but we may mention in passing one very interesting generalization. The various atoms have atomic weights of either $4m$, $4m+1$, $4m+2$ or $4m+3$, where m is a whole number. Examples of the three types would be carbon of mass 12 (i.e., 4×3), carbon of mass 13 ($4\times3+1$), nitrogen of mass 14 ($4\times3+2$) and nitrogen of mass 15 ($4\times3+3$) (See also Chapter III). It is interesting to note that the facts of spectroscopy require, in general, that the nuclear spin be 0 if the atomic weight is $4m$, 1/2 if the atomic weight is $4m+1$, either 0 or 1 (usually) if the atomic weight is $4m+2$ and 3/2 if the atomic weight is $4m+3$. For elements of high atomic weight these rules are not exactly obeyed and some nuclear spins seem to exceed 3/2 unit. It is obvious that the rules of vector addition may apply to the nucleus as well as to the planetary electrons. In fact this suggestion has been used to arrive at very interesting conclusions regarding atomic stability and abundance.

IX. The New Quantum Mechanics

We have already pointed out some of the difficulties which the Bohr atom encountered. Others should be given in order that one may understand the reasons for the substitution of the so-called New Quantum Mechanics. In the Bohr atom a few ideas of classical mechanics were coupled with a few quantum postulates to arrive at a picture which, to say the least, lacked homogeneity. No idea was given at all as to the mechanism by which an electron changed from one state to another. It was supposed to disappear from one state and appear in another without any knowledge of its intermediate history being available. Furthermore the intensities of spectral lines could not be calculated by means of the simple Bohr Theory. If one wishes to calculate the intensity of sound waves emitted by a tuning

fork one needs to know the amplitude with which the tuning fork is vibrating. Similarly for electromagnetic waves one needs to know something of the amplitude of the emitter. The Bohr theory as originally proposed contained no amplitudes of any sort. It became necessary, therefore, to introduce a *correspondence principle.* Just as the classical theory led to a formula for black body radiation which was quite satisfactory for long wave-lengths, so the Bohr atom was supposed to approach a classical emitter for high quantum numbers and small changes in quantum number. By use of this correspondence between an emitter which obeyed classical mechanics and the Bohr atom which obeyed quantum mechanics it was possible to calculate the intensities of spectral lines. The method left much to be desired from the standpoint of pure logic and in addition theory did not always agree well with experiment.

The Bohr theory was also unable to account quantitatively for the effect of a magnetic field on the emission of spectral lines, for the helium spectrum and for the scattering of slow moving electrons by gas molecules. All of these differences between theory and experiment coupled with the looseness of the principles of the Bohr theory prepared the scientific world for the advent of new, more satisfactory ideas.

In 1923 a French physicist, Louis de Broglie, suggested that a moving particle might be treated by the same type of mathematics that one uses ordinarily in dealing with wave motion. We have already seen that Einstein assumed that quanta could be treated as moving particles in explaining the photoelectric effect. Compton had shown also that an x-ray quantum could be considered as a particle in some instances. If an x-ray quantum encounters an electron it bounces off in one direction with diminished energy and the electron acquires part of the energy. Compton's calculations involved the laws of conservation of energy and conservation of momentum, the momentum of a quantum being its

energy ($h\nu$) divided by the speed of light, or $h\nu/c$. Since frequency divided by the speed of light is the reciprocal of wave-length, Planck's constant divided by wave-length is equal to momentum. De Broglie merely suggested that a moving particle may be treated in the same way, that is, its "wave-length" will be equal to Planck's constant divided by its momentum (mass × velocity).

We are not able to form any very definite picture as to the nature of such "particle waves." They are certainly not electromagnetic. Perhaps it is best to state merely that by associating a wave-length with a moving particle one arrives at formulae which satisfactorily account for many different phenomena. Thus Davisson and Germer, G. P. Thomson and others have shown that moving electrons show interference in a manner exactly comparable to x-rays and Dempster has demonstrated a similar phenomenon for moving protons.

De Broglie used his postulate to derive a formula for the hydrogen spectrum without, however, throwing out many of the essential features of the Bohr atom. Instead of the Bohr quantum postulate that circumference times mass times velocity is a multiple of the Planck constant h, de Broglie assumed that only those states are possible in which the circumference divided by the wave-length of the electron is a whole number. This obviously leads to the same formula as that obtained by Bohr, since circumference divided by wave-length, or circumference times mass times velocity divided by h is to be a whole number n. This statement is evidently exactly equivalent to equation (2) on page 54. n has a different significance from that given to it by Bohr since it has become now the number of *electron wave-lengths* contained in the circumference of the orbit.

This theory in its elementary form, in spite of its interesting character, did not solve many of the difficulties inherent in the Bohr theory. It remained for Schrödinger to place the theory in a more useful, although certainly more ab-

stract, form. Schrödinger incorporated the wave-length of particle waves in the classical equation for wave motion and obtained thereby an equation of outstanding usefulness. In fact this equation would seem to have, on its surface, little justification other than its utility. It has, however, been shown that it may be used to attack subatomic problems with great success.

Instead of adopting a quantum postulate which limits strictly the number of energy states in which an atom may

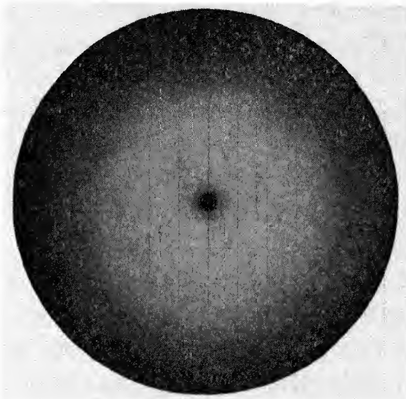


FIG. 6. Probability distribution of an electron about the nucleus of a hydrogen atom in the normal state. (After Dushman. Reprinted by courtesy of the *Journal of Chemical Education.*)

exist, the new method is to solve the wave equation for energy values. It is found that the solutions of the equation lead to the same energy values as the Bohr theory in such cases as the Bohr theory gave correct results, and that it is in agreement with experiment in all cases, even when the Bohr theory led to the wrong result. The picture of the atom is somewhat vague, although there occurs in the equation a certain function, the *proper function* (eigenfunktion) which may be diagrammed as a function of the distance from the nucleus of the atom. Attempts have been made to relate this proper function to electron density, but properly speaking we treat merely with a highly useful function

whose characteristics determine the nature of atoms. If any picture of the atom is possible it is statistical in character. Thus we determine the probability (or the fraction of the time) that the electron will be at a certain distance from the nucleus. It may sometimes wander far afield and may sometimes be very close at home, but we can only describe its average behavior and not locate it at any particular instant. Fig. 6 shows a picture diagram of this sort of distribution in which the probability of occurrence of the electron is greatest in the light portions.

X. Heisenberg's Uncertainty Principle

Prior to the advent of the Schrödinger theory, Heisenberg had developed a mathematical method of treating atomic problems. It has been shown that the two methods are really identical in all but the type of mathematics used. The Heisenberg theory was, if anything, more abstract than the other and lends itself even less readily to pictorial representation. We need not discuss here the broad outlines of this theory for it leads to much the same results as Schrödinger's. Heisenberg has introduced, however, one famous principle, the Uncertainty Principle or Principle of Indetermination.

The principle of indetermination tells us that we may never hope to determine both the momentum and the position of a particle with unlimited precision. In fact the uncertainty in the position multiplied by the uncertainly in the momentum will always be at least as large as Planck's constant. This means, that if we know exactly where an electron is we know nothing at all about its momentum. Much philosophical speculation has been founded on this principle, but ideas emanating from it are frequently overdrawn. This principle does not prohibit us from using picture models which seem to place the electrons in definite positions if such pictures are useful, but it does tell us that any mathematical development based on such precise pic-

tures is foredoomed to failure. In fact we may have here one of the chief difficulties with the Bohr theory.

The net result of the aspects of quantum mechanics which we have passed over rapidly in the last few paragraphs is that we claim to know less than we did about the precise nature of things, in fact we realize that there is a definite limit beyond which we may never hope to pass. We content ourselves with statistical pictures which enable us to predict on the average what is going to happen but admit our ignorance of the exact state of things at the present or any past time. In fact we are coming to realize that the question as to whether a given theory is right or wrong is largely meaningless when we are dealing with electrons, atoms and molecules. We only demand that the equations resulting from the theory shall accurately describe the results obtained in the laboratory.

VI. The Chemist's Atom

Thus far we have confined ourselves largely to the point of view of the physicist.

The chemist, however, has a large mass of evidence which must also be accounted for by any theory of atomic structure. The data are just as precise in their way as those of the physicist, but they have been less adaptable to mathematical treatment.

We may summarize the data which an atom model must satisfy in order to please the chemist:

(a) The periodic classification of the elements.

(b) The valence of the elements.

(c) Electropositivity and electronegativity as defined in terms of chemical reactions.

(d) The carbon atom in particular must satisfy the demands of organic chemistry with regard to problems of isomerism, etc.

It has been said many times that the chemist's atom differs from the atom of the physicist. This is not true of

course. Chemists have been less concerned until recently with precise mechanical pictures. From many standpoints it is immaterial to them whether the electrons are in motion or not.

The so-called static atoms of Lewis, Kossel, Parson, Langmuir and others were designed to give a qualitative picture of chemical phenomena. It is obvious that theories of physicists and chemists cannot permanently disagree.

Of the facts used in arriving at atom models by chemists, those concerned with the periodic table are of greatest importance. Since the periodicity at the beginning of this table is one of eight, this number played an important role. We may list the second to the seventeenth elements in a table, putting those with similar chemical properties in the same vertical column. Hydrogen of atomic number one and atomic weight 1.008 really belongs by itself. The next sixteen elements are as follows:

Element	Helium	Lithium	Beryllium	Boron
At. No.	2	3	4	5
At. Wgt.	4.00	6.92	9.02	10.82
Element	Carbon	Nitrogen	Oxygen	Fluorine
At. No.	6	7	8	9
At. Wgt.	12.00	14.01	16.00	19.00
Element	Neon	Sodium	Magnesium	Aluminum
At. No.	10	11	12	13
At. Wgt.	20.2	23.00	24.32	26.97
Element	Silicon	Phosphorus	Sulfur	Chlorine
At. No.	14	15	16	17
At. Wgt.	28.06	31.03	32.06	35.46

Helium and neon, elements 2 and 10 respectively, are very inert from a chemical standpoint. Lithium and sodium are very electropositive, that is they tend to give up electrons easily to other elements to form compounds. For example, one atom of lithium or sodium will react with one atom of chlorine to form compounds of the type LiCl or NaCl in which the chlorine is negative (having acquired an electron) and the lithium and sodium atoms positive (having lost electrons).

Beryllium and magnesium are also quite electropositive. They form compounds of the type $BeCl_2$ and $MgCl_2$. Boron is less electropositive, although aluminium is quite decidedly so. They form compounds of the type BCl_3 and $AlCl_3$. Carbon, silicon, and nitrogen cannot be spoken of as positive or negative in the same sense as the preceding elements because of their tendency to share electrons with other atoms (See Chapter IV). Oxygen and sulfur unite with metals such as lithium or sodium, presumably taking electrons away from the latter. Fluorine and chlorine react with metals and many other substances readily, usually forming negative ions, or sharing a pair of electrons.

There is a regular change in valence as we proceed across the list. A consideration of this fact led Lewis to propose the so-called *octet theory*.

Since helium is inert the configuration of the helium atom must be a stable one. Its atomic number is two and there must be two electrons outside of the nucleus.

With lithium, which tends to give up one electron easily to chlorine, one of the three electrons must be farther from the nucleus than the other two. With beryllium there would be two easily removable electrons.

Since neon is also an inert gas, the configuration of the neon atom must be a stable one. It might be represented with two electrons relatively near the nucleus (corresponding to the two helium electrons) and eight electrons symmetrically arranged outside.

Carbon might form a neon structure by sharing four pairs of electrons, nitrogen by sharing three pairs, oxygen by sharing two pairs and fluorine by sharing one pair. Nitrogen, sulfur and iodine may become a part of a positive ion by sharing four, three or two pairs of electrons.

This picture of the atom satisfies the simple rules of valence very satisfactorily. Since the periods in the periodic table are not eight after the second period but are 18, 18, 32, 8, it is necessary to modify in some manner any simple

picture based on the octet. The rare gases, helium, neon, argon, krypton, xenon and niton are all stable configurations. An element following a rare gas always has a valence of $+1$ and each element preceding a rare gas may have a valence of -1. The general basis of the theory is similar to that given above for the first two periods.

Probably the most important idea contained in the Lewis theory was that of the electron pair. When two atoms enter into combination either one atom gives an electron to the other (generally resulting in an even number of electrons being possessed by each atom) or the atoms share a pair of electrons which, according to the theory, is situated between them. The electron pair is also inherent in the vector model of the atom and the picture of valence obtained from the new quantum mechanics is also in agreement with it. According to the vector model each electron possesses a spin. When electrons are added together to form atoms the vast majority of them are paired off in such a way that the net spin is zero. In other words for each pair of electrons the spin of one is in the opposite direction from the spin of the other. Similarly when two atoms combine, the uncoupled spins of the electrons of one atom pair off with the uncoupled spins of the electrons in the other atom. For example sodium with a valence of one will have one electron whose spin cannot be coupled with anything. Chlorine with seven valence electrons will have six grouped in three pairs and one left over. When sodium chloride is formed the valence electron of the sodium is given to the chlorine atom, its spin neutralizing the spin of the seventh chlorine electron. Thus two ions are formed for each one of which there is no electron spin unneutralized. When we consider the elements with two valence electrons (magnesium, calcium, mercury, etc.) the picture is somewhat more complicated. In the normal state of such an atom the spins of the two valence electrons neutralize each other. In the act of chemical combination the spins of these two electrons must be uncoupled, each one neutralizing the spin of some electron

of the atom with which reaction occurs. In a certain sense, therefore, one might say that the normal valence of such atoms is zero, but that since the spins are relatively easily uncoupled there is an excited state in which the valence will be two.

The new quantum mechanics looks at the whole matter in a somewhat different way. Here the problem is to determine the change in distribution of the proper functions (eigenfunktions) for the two atoms as they are brought together. In this manner Slater, Pauling and others have succeeded in arriving at conclusions which are in entire agreement with the facts of chemistry. Thus the four hydrogens in methane are found to be located at the corners of a tetrahedron, thereby giving a picture which accounts for the facts of isomerism. Interesting and important conclusions may be expected from the application of quantum mechanics to chemical problems, not the least of which will be in the field of chemical kinetics, dealing with the rates of chemical transformations.

XII. Ortho and Para Hydrogen

One other problem may be discussed in passing, since its solution involves the use of the new mechanics. We will use the vector model. We have mentioned already that nuclei possess spin. There are two ways of forming a hydrogen molecule from two hydrogen atoms. Either the nuclear spins will neutralize each other (be anti parallel) or they will not (be parallel). In the former case we shall have what is commonly called para hydrogen and in the latter ortho hydrogen. (The use of the terms *ortho* and *para* is not to be confused with their use in organic chemistry.) Ordinary hydrogen (H_2) will consist of a mixture of the two forms, three parts of ortho to one part of para. Other things being equal the modification with no net spin will have less energy than the other so that at very low temperatures hydrogen will be almost entirely in the para form. Bonhoeffer has made use of this fact to prepare 99.7 per cent pure para hy-

drogen. In the absence of a catalyst such as charcoal the rate of change from one form to the other is slow, so that ordinary hydrogen cooled rapidly in an ordinary vessel will still contain the three to one mixture. Cremer and Polanyi have shown recently that the change from one form to the other takes place with measurable speed in solid as well as in liquid hydrogen. It seems unlikely that pure ortho hydrogen will ever be prepared for the three to one mixture is the stable one at all temperatures above room temperature.

The property of possessing symmetrical and antisymmetrical forms is common to all molecules composed of like atoms which possess nuclear spin.

One could continue to list the fields in which the new quantum mechanics has been applied with remarkable success. It is hoped that the above brief presentation will give to the reader something of the viewpoint of what is frequently called the newer physics.

References

Bridgman, P. W. "Permanent elements in the flux of present-day physics." *Science*, 1930, **71**, 19.

Thomson, Sir J. J. *The corpuscular theory of matter.* New York: Charles Scribner's Sons, 1907.

Bohr, N. *The theory of spectra and atomic constitution* (three essays). Cambridge: University Press, 1922.

Sommerfeld, A. *Three lectures on atomic physics.* New York: Dutton.

Haas, Arthur E. *Die Welt der Atome.* Berlin: De Gruyter, 1926. [*Atomic theory.* Translation by T. Verschoyle. London: Constable.]

Condon, E. U., and J. E. Mack. "An interpretation of Pauli's exclusion principle." *Phys. Rev.*, 1930, **35**, 579.

Thomson, G. P. "Waves and particles." *Science*, 1929, **70**, 541.

Lewis, G. N. *Valence and the structure of atoms and molecules.* New York: Chemical Catalog Co., 1923.

Lewis, G. N. *The anatomy of science.* New Haven: Yale University Press, 1926.

Chapter III

THE TRANSMUTATION OF THE ELEMENTS: THE PHILOSOPHER'S STONE

It is only human to desire wealth and the power over one's fellow beings which may be obtained with it. In our minds wealth is associated with gold, or with certificates which may be exchanged for gold and we lose sight, all too frequently, of the fact that gold of itself is valueless unless it may be exchanged for commodities which are useful to us. In a capitalistic civilization, however, the acquisition of gold implies the increase in the ability to acquire the goods of the world and it is not to be wondered that cheap methods of producing gold formed one of the chief objects of the researches of the predecessors of the modern chemists. In this they were encouraged by the medieval nobility, to whom gold meant ability to maintain armies and acquire power. It is, perhaps, a great sign of progress that chemists have changed their object from the production of gold with which to buy goods to the betterment of the production of the goods themselves.

The hopes of the Middle Ages have not been converted into the realities of today, although we feel that we know more concerning the laws of Nature and realize some of the difficulties which have prevented the artificial transmutation of the elements. Few attempts to cause artificial conversion of one element into another have led to positive results. This statement needs some amplification in what follows, but it stands as essentially correct if one uses the proper definition of the word artificial.

In the chapter on Atomic Structure, mention has been made of the spontaneous transmutation of the radioactive

elements. These elements all possess high atomic weights, with the exception of rubidium and potassium, and they are not abundant on the surface of the earth. The laws governing radioactive transformations were discovered one by one experimentally and only in recent years has any success been attained in deriving these laws with the aid of Quantum Mechanics.

It cannot be emphasized too strongly that human beings have no control over radioactive transformations. Attempts to increase the rate of decay of a radioactive element by heat or to slow it down by cold have been uniformly unsuccessful. In this respect, as well as in others, these transmutations differ from ordinary chemical reactions. The rate of inversion of cane sugar increases nearly three-fold for a rise in temperature of ten degrees centigrade and this same phenomenon is quite universal, but the rate of decay of radium is the same at several thousands degrees above zero as it is at the temperature of liquid air, nearly two hundred degrees below zero. An increase in temperature means an increase in the energy of movement of molecules, and it is of great significance that such increases in kinetic energy have no effect on radioactive atoms. This would seem to mean that the phenomenon of radioactivity is to be ascribed to some part of the atom which is not affected by collisions with its neighbors.

This brings us to another essential difference between ordinary chemical reactions and radioactive changes. Let us merely consider such a human phenomenon as that of marriage. In the United States, at least, the engagement of a young couple only follows the proper kind of an encounter between a young man and a young woman. In a man's college no engagements would result, in the absence of contacts with the outside world. In a coeducational institution, as long as the number of men is equal to the number of women, the number of engagements per year should depend on the enrollment. If the number of women is doubled,

but the number of men kept constant, the number of engagements should increase, but it could only double if the number of engaged persons was a small fraction of the total. The chance that a man will encounter a suitable girl will be proportional to the number of girls he encounters and the chance that a girl will meet the right man will vary directly as the number of men she encounters. With a small fraction of engaged couples, therefore, doubling the number of men and the number of women should lead to four times the number of engagements. Now this is exactly what does not happen with radioactive elements. The number of reactions is independent of the number of encounters with neighboring atoms and the same fraction of a gram of radium will decompose per second whether it is in one lump or distributed uniformly over the entire surface of the earth. In this way radioactive decay would be more nearly analogous to divorce, providing, of course, that divorce resulted only from incompatibility and was never occasioned by outside persons.

In a previous chapter (p. 43) mention has been made of the "building blocks" from which atomic nuclei may be constructed. These building blocks, protons, electrons and alpha particles (which themselves may be built of protons and electrons) must be held together in stable configurations in most of the elements. In the radioactive elements there must be a measure of instability which varies greatly from one element to another. If the atoms are unstable why do they not all decompose at once? We know that when they do decompose they liberate enormous amounts of energy. A mixture of hydrogen and oxygen may be kept for some time, but when reaction is started it results in an explosion with the production of a large amount of heat. Why is this not true of radioactive elements?

Theories of nuclear disintegration have, in the past, been exceedingly vague and have, in reality, done little more than tell us in different language what we already knew. In

a certain sense this is true of the application of the newer forms of Quantum Mechanics to radioactivity, but the type of language is now so universal in solving diverse problems that we have a feeling, at least, that we are capable of understanding the nucleus as well as we understand anything else in the field of subatomic physics.

Let us return to the mixture of hydrogen and oxygen. The system is unstable. We may picture it as water lying in a valley of high altitude separated from the ocean by a mountain range. The water could be syphoned out into the ocean, but in order to do this we would have to exert sufficient pressure to get the water started over the mountain range. The pressure we must exert to get the process started would be somewhat analogous to the spark which starts the explosion of our mixture.

Now anyone can understand the mechanical analogy which has just been used to "explain" what is, in reality, a very obscure phenomenon unless one uses the language of the new Quantum Mechanics. The initial boost which starts a process off may come from many sources for an ordinary chemical system such as our mixture of hydrogen and oxygen. We may use a spark, or shine ultraviolet light on the mixture, or use a detonating cap, or warm the mixture up and in every case we get the same result—an explosion. But in the case of the radioactive atoms we are not able to do anything which helps the process along and yet we know that the "syphon" should work because we can obtain energy from our system. Is it that our feeble efforts at exerting the initial pressure are altogether inadequate to force the water to the top of the divide, or must we use a different language to describe the phenomenon?

Not alone are we unable to do anything to push the water to the top of the divide for radioactive changes, but it is difficult for us to imagine any mechanism by which the proper pressure could be exerted. Here the new Quantum Mechanics comes to our rescue. We have pictured a solid

mountain so that the water could only get on the other side by going over the top. The new ideas permit the water to leak through. In fact they go a little further and enable us to calculate the chance of finding water on the two sides of the mountain. Obviously if the water can ever get on the ocean side of the mountain all it has to do to get away is to run down hill.

Our picture of radioactive decay is still vague but has a certain philosophical pleasantness, for we merely find that a difficulty no longer needs to be considered if we talk the right language. To put the matter crudely, let us imagine an alpha particle associated with the nucleus of some atom. Both the alpha particle and the nucleus are positive and they would normally repel each other and fly apart. Something or other prevents this from happening, or in other words the alpha particle is still in the valley. The particle may wander around, however, and there is a small, but definite, probability, that it will find itself across the mountain, that is it may "leak through" the potential barrier which holds it in. When it gets on the other side by mere chance the repulsion between it and the rest of the nucleus sends it flying away and a radioactive decomposition results. Now this vague description is only vague because we are not using mathematics. In mathematical form the theory is found to be quite beautifully applicable and to lead to the beginning of what will probably be some day a complete explanation of radioactive phenomena.

To carry our theory one step further, the reason uranium decomposes slowly (one-half of it decomposes in ten billion years) and Radium C decomposes more rapidly (one-half in a millionth of a second) is that their probability functions differ. This may sound self-evident and not appear to be an explanation at all, but the generalizations which may be obtained for the radioactive families lend a certain reasonableness to the entire method of calculation.

The same sort of picture which we have just used to

describe the ejection of alpha particles must also be used for the ejection of beta particles (electrons), although here there should exist an attraction between them and the positive nuclei from which they are ejected.

We need not repeat here the essential facts which have been used to fit the radioactive elements into families. It is of more interest for us at present to consider the possibilities of producing atomic transmutations in elements which are not normally radioactive.

Radioactive changes are all connected with the nuclei of atoms. Alpha particles are helium nuclei, that is they have an atomic weight of four and a positive charge of two. Therefore when an atom loses an alpha particle its atomic weight decreases by four and its atomic number by two. Similarly beta particles are electrons, having relatively small masses on the atomic weight scale. The ejection of a negative charge is the same in net effect as the addition of a positive charge. Consequently when an atom loses a beta particle its atomic weight does not change since the increase in the positive charge on the nucleus means that the atom must acquire one more planetary electron. The atomic number has, however, been increased by one.

We have already mentioned that the various radioactive elements do not all decay at the same rate. When we speak of chemical systems we know that of two unstable systems the one which is most unstable will give up the most energy upon reaction. The same generalization might apply to radioactive elements, that is those which are most unstable should give out the most energy when they decay. Thus the elements which decompose most rapidly would be expected to eject alpha particles of greatest speed. This is found to be true. A similar law is valid for the ejection of beta particles.

The speeds of alpha particles vary from one element to another, but are approximately one tenth to one twentieth of the speed of light or ten to twenty thousand miles per second. The speeds of beta particles are much greater, in

some cases closely approaching the speed of light. However the mass of the alpha particle at rest is more than seven thousand times as great as that of the electron at rest. Since kinetic energy is equal to one half the mass of the moving body multiplied by the square of the velocity ($1/2\ MV^2$), at the same speed an alpha particle will have more than seven thousand times the kinetic energy of a beta particle. This statement is true as long as the speed of the particle does not approach the speed of light, but the Einstein theory of relativity tells us that the apparent mass of a moving body increases with its speed according to the formula $M = M_0/\sqrt{(1-V^2/c^2)}$, where M is the mass at the velocity V, M_0 is the mass "at rest" and c is the speed of light. When the speed of the particle is equal to the speed of light we have $1-c^2/c^2=0$ and the value of the mass is infinite. Thus the apparent mass of a beta particle having a speed nearly equal to that of light may be very large and its kinetic energy may be large. Actually the kinetic energy approaches M_0c^2 at the speed of light. As soon as it loses part of its energy through collisions with molecules its mass becomes smaller.

Attempts to produce artificial transmutations of the elements have nearly all been unsuccessful. However alpha particles (and perhaps beta particles) with their exceedingly high kinetic energies are capable of producing changes in atoms which they encounter.

The path of an alpha particle in passing through a gas may be made easily visible by a device first employed by C. T. R. Wilson of Cambridge University. Let us consider an evacuated cylinder fitted with a piston and containing only water vapor. As we compress the water vapor by moving in the piston the pressure will increase. Nothing will happen other than a pressure increase until the pressure equals the vapor pressure of liquid water at the temperature at which we are carrying on the experiment. At this point droplets of liquid water are produced and further movement

of the piston leads to no increase in pressure but merely increased condensation of the water vapor to form liquid water. Or we could carry out an experiment in a different manner. We could keep our piston in a fixed position and cool down the cylinder. When the "dew point" is reached liquid droplets will appear on the walls. Now these experiments have been described as though we were dealing with an ideal system, that is one which is always in equilibrium. Fortunately water vapor will not behave always in the manner just described. Unless something is present on which the water may condense a high degree of supersaturation may be attained. Dust particles or gaseous ions (charged molecules and atoms) may serve as nuclei for condensation.

When alpha particles pass through a gas they produce large numbers of ions. If, now, the gas is supersaturated with water vapor myriads of water droplets are produced in such a manner that they indicate very clearly the path which the alpha particle followed. This, in brief, is the principle of the C. T. R. Wilson apparatus. A cylinder is fitted with a piston, but instead of compressing the gas to obtain the desired supersaturation, it is suddenly expanded and thereby cooled. The paths of the alpha particles may be photographed if they are suitably illuminated (See Figs. 7 and 8).

Atoms behave as though they were very loose systems, that is they seem to contain a lot of empty space. Alpha particles in passing through atoms may ionize them, but they are little affected themselves in the process. The electrons they cause to be ejected from the atoms and molecules through which they pass are very light and can be removed without the expenditure of large amounts of energy. Consequently the direction of flight of the alpha particle is little changed by producing ionization and its loss in energy is gradual. Alpha particles may travel several centimeters in air.

The nuclei of atoms are very heavy, but they seem to

occupy very small volumes. The chance that an alpha particle will hit the nucleus of an atom is very small. It is as though a blind marksman were shooting at a target several feet in diameter with a bull's-eye less than an inch across. The chance of hitting the bull's-eye would be pretty remote. Consequently even though an alpha particle may pass through millions of atoms it very rarely comes close to the nucleus. This means that the observation of a large number of alpha ray tracks would be necessary before, on the average, one could be found in which a nucleus had been hit. Fortunately such observations can be made, for several investigators have attached moving picture cameras to Wilson cloud track apparatuses in such a way that pictures may be taken fairly rapidly. Thus hundreds of thousands of pictures showing millions of alpha ray tracks have been made.

In any collision between two bodies two fundamental laws must be obeyed: (1) The law of conservation of energy. That is, the sum of the energies of the particles after collision must be equal to the sum of the energies before collision. (2) The law of conservation of momentum. That is, the sum of the forward components of the momenta of the particles after collision must be equal to the initial momentum of the alpha particle. Momentum is the product of mass by velocity.

As we have pointed out above, alpha particles pass through large numbers of molecules without suffering appreciable changes in direction. Occasionally, however, the path of the alpha particle is bent sharply at some point, thus indicating that a collision between the alpha particle and some heavy body has taken place. These collisions may now be classified into two types: (1) Those in which the laws of conservation of energy and conservation of momentum are obeyed obviously. That is, the alpha particle bounces off in one direction and the atom which has been hit moves off in another and the whole phenomenon may be treated mathematically as though a light swiftly moving ball had hit a heavy ball

previously at rest. These collisions are termed elastic and there is nothing mysterious about them (See Fig. 7). (2) Very rare collisions are observed in which the application of the laws of conservation of energy and momentum is not at all obvious. Here something peculiar seems to have happened which cannot be treated by simple analogy to a collision between two balls.

Most of the collisions of the latter type have been observed in nitrogen (See Fig. 8). Here the phenomenon may be described as follows. The alpha particle probably hits a nitrogen nucleus, but the alpha particle seems to cease to have an independent existence at this point for no track corresponding to it can be observed following the collision. There are, however, two tracks leaving the point of collision. One is very faint and quite long, the other shorter but much heavier. The first seems to correspond to a proton traveling with high velocity and the other must be due to the residue of the atom which has been hit. Since no track due to the alpha particle is visible it must have combined with the atom with which it collided.

The results of the collision may then be summarized in the following manner. The atomic weight of nitrogen is 14 and the atomic number is seven. Removal of one proton would leave an atom of weight 13 and charge six, but since the alpha particle is to be added on we have a weight of 17 and a nuclear charge of 8. The atomic weight of oxygen is usually considered to be exactly 16 and the atomic number 8. The formation of an isotope of oxygen seems to have taken place at the time of the collision of the alpha particle with nitrogen. This is, therefore, a species of atomic transmutation but it could scarcely be called artificial.

The existence of oxygen atoms of mass 17 was unknown until quite recently. Their detection by ordinary means would be difficult due to the presence in all gas discharges of traces of water vapor which might break down to give OH groups (molecular weight 17.008). However, Giauque and

Johnston in analyzing the so-called atmospheric absorption bands of oxygen, which had been measured with high precision by Babcock, did detect lines which could be ascribed

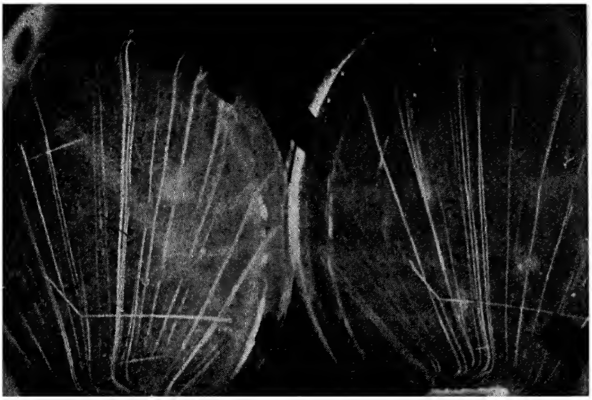


FIG. 7. Elastic collisions in nitrogen.*

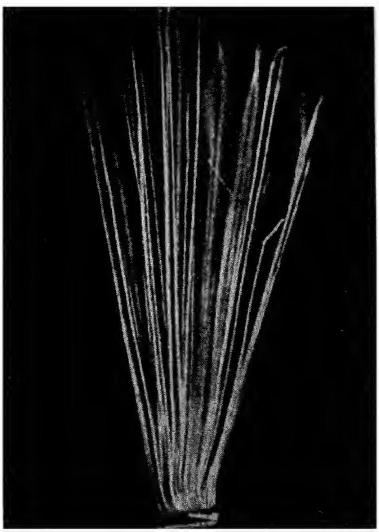


FIG. 8. Atomic disintegration and synthesis.*

* Courtesy of Professor Harkins.

to molecules formed by the addition of one oxygen atom of mass 16 to one oxygen atom of mass 17. Since radioactive substances have been shooting alpha particles into nitrogen during the geologic ages the formation of appreciable quantities of oxygen atoms of mass 17 would be possible. Whether this process would account for the quantity now known to be present is open to question.

One further interesting hypothesis has been advanced by Urey. He has carried out detailed calculations on seven collisions of the type we are discussing and has come to the conclusion that three types of oxygen atom having the atomic weights 17.00504, 17.00322 and 17.00135 respectively have been formed. This, he suggests, may be due to different energy levels within the oxygen nuclei. This is an interesting speculation and opens up the whole question of such energy levels from a new angle.

The question naturally arises as to whether elements other than nitrogen may not be decomposed by alpha particle bombardment. This question may be answered definitely in the affirmative. Chadwick in Rutherford's laboratory at Cambridge University and Kirsch and Pettersen at Vienna have made a large number of studies along these lines. Instead of using the Wilson cloud-track apparatus, they have found it more convenient to study the scintillations produced on a properly prepared zinc sulfide screen by the flying protons. These ejected protons will, in general, travel much further through air than alpha particles so that it is possible to observe their effects without ambiguity. There is some disagreement between the conclusions reached at these two laboratories, but both find a large number of elements to give out protons when bombarded by alpha particles.

We have made mention previously of the fact that nature seems to prefer even numbers. As regards atoms she seems to prefer those whose atomic weights are divisible by four and whose atomic numbers are divisible by two. Such atoms,

we may say, have atomic weights $4m$ where m is a whole number. Examples are helium (4), carbon (12), oxygen (16), etc. Other elements will have atomic weights $4m+1$, for example beryllium (9), oxygen (17), neon (21). Still others will have atomic weights $4m+2$ (lithium, 6, nitrogen, 14, etc.) and finally some will correspond to $4m+3$ (lithium, 7, aluminum, 27, etc.). Now those elements whose atomic weights are given by $4m$ decompose rather rarely and when they do they seem to give very short range protons. Those with atomic weights $4m+1$, $4m+2$ and $4m+3$ decompose much more frequently and give much longer range protons. In fact aluminum gives protons which will travel more than a yard through air. Thus we find that the stability rules of Harkins are quite applicable to this type of atomic disintegration and synthesis.

Attempts to cause transmutation of the elements by other methods are numerous. One of the most fascinating speculations has to do with the conversion of hydrogen into helium. Hydrogen, on the atomic weight scale, has a mass of 1.008, whereas helium has an atomic weight of 4.000. Four atoms of hydrogen could combine to form helium with a loss in weight corresponding to 0.032 atomic weight unit. Since by the theory of relativity mass and energy are interconvertible, this loss in weight might take place by the emission of energy. In fact the evolution of energy should be so large that if equilibrium were established all of the hydrogen in the universe would be converted into helium. This process of helium formation has been advanced as an explanation for the heat of some of the stars, but attempts to observe it under laboratory conditions have all met with failure.

At this point mention may be made of the so-called cosmic radiation which has been studied by numerous investigators. This radiation is of exceedingly short wave-length, shorter even than the gamma rays emitted by radioactive substances. It is extremely penetrating and the effects of it may be observed after passage through many feet of water.

It is omnipresent and seems to reach the earth from interstellar space.

The determination of the wave-length of cosmic radiation can only be made by approximate methods. The variation in penetrating power of x-rays and gamma rays as a function of wave-length has been carefully studied. By extending the formulae an approximate idea of the wave-length of cosmic radiation may be obtained from its penetrating power.

Various theories of the origin of cosmic radiation have been advanced. Millikan is of the opinion that it is emitted during processes of atomic synthesis. That is, when sufficient protons and electrons have grouped together to form an iron atom, for example, they "condense," emit a cosmic ray and the iron atom is produced. There are numerous objections to this sort of theory, not the least of which is in understanding the mechanism whereby sufficient protons and electrons could get together at one time in interstellar space. Jeans, on the other hand, believes that cosmic radiation may be due to the annihilation of helium or hydrogen atoms, that is, the protons and electrons disappear and the matter lost appears as radiant energy. The recent work of Compton in measuring the intensity of cosmic radiation at various latitudes indicates that the intensity is smallest at the equator and increases as one proceeds toward the magnetic poles. This is difficult to explain unless cosmic rays consist of charged particles which are affected by the magnetic field of the earth. Whatever the true explanation of the origin of cosmic radiation, a fruitful field for speculation has been opened up by their discovery.

Attempts to cause transmutation of the elements by artificial means are numerous. The element which the alchemists wished to obtain was gold. It has an atomic number of 79, the fact that it is not an even number agreeing well with its rarity. The atomic number of mercury is 80. Theoretically one could transform an atom of mercury into an atom

of gold by either removing a proton or adding an electron to its nucleus. German investigators have reported the formation of gold in mercury used in mercury arc lights. It would be very surprising, however, if an electron could be added to a mercury nucleus under such mild conditions as obtain in the mercury arc, for the planetary electrons of the mercury would act as a very efficient protective coating. Further and more careful work, even with very high speed electrons, has failed entirely to confirm the earlier work. The difficulty seemed to be in obtaining mercury which was entirely free from gold.

Several investigators have passed exceedingly high currents through very fine wires, thereby causing a sudden vaporization or explosion. Certain ones reported that tungsten wires could be converted into helium in this manner, but here again more careful experimentation has yielded entirely negative results.

Still other workers reported that the presence of nitrogen on the surface of the wire was a necessary condition for obtaining helium. In fact neon as well as helium was found. However the test for helium is so delicate that entrance of the merest trace of air into the apparatus would give an apparently positive result. Here again confirmation of the positive results is lacking.

Recent experiments in the Cavendish Laboratory at Cambridge University indicate that when lithium (At. wgt. 7) is bombarded with hydrogen ions (protons of atomic weight 1) formation of helium may take place. At least the hydrogen seems to disappear and we appear to be confronted with a real, *bona fide*, transformation of one element into another. Surprisingly little energy seems to be necessary for the initiation of the process, of the order of 100,000 volts. Recent attempts to produce very high potentials, capable of imparting to charged particles kinetic energies approaching those of alpha particles, have met with some success. Thus a new and powerful tool is now available for attempting arti-

ficial transmutations.

In the past few months the formation of *neutrons* has been indicated in experiments in which certain elements are bombarded by alpha particles. The neutron would be a particle without charge and presumably of mass 1 on the atomic weight scale. The absence of charge makes the detection of neutrons difficult. They do produce ionization, however, since they are ejected with high velocities. The nature of the neutron is uncertain, but it seems doubtful whether it consists of a proton and an electron in very firm combination. Recent work shows also that there may be a *positive electron*, not the proton, having a mass similar to that of the known negative electron. Indeed the suggestion has been made that the nucleus of the hydrogen atom may consist of a neutron plus a positive electron. It seems certain that our ideas concerning nuclei may soon undergo important revision.

References

Fajans, K. *Radioaktivität.* Braunschweig: Friedr. Vieweg und Sohn, 1922.

Lind, S. C. *The chemical effects of alpha particles and electrons.* New York: Chemical Catalog Co., 1928.

Harkins, W. D., and E. D. Wilson. "The changes of mass and weight involved in the formation of complex atoms." *Jour. Am. Chem. Soc.*, 1915, **37**, 1367. (See also pp. 1383, 1396.)

Harkins, W. D., and A. E. Schuh. "The frequency of occurrence of the disintegrative synthesis of Oxygen 17 from Nitrogen 14 and helium." *Phys. Rev.*, 1930, **35**, 809.

Rutherford, Sir E. *Radioactive substances and their radiations.* Cambridge: University Press, 1913.

Rutherford, Sir E., James Chadwick, and C. D. Ellis. *Radiations from radioactive substances.* Cambridge: University Press.

Chapter IV

VALENCE

I. Historical Background

When any theory is followed through its historical development, it will be found, usually, that many diverse elements have entered into its formation. While there is some simple idea which persists, it has often happened that the principle was not clearly recognized at first and that other related discoveries have been made without an immediate recognition of the relation. Sometimes parts of the principle have been accepted for a time, then abandoned and later revived in an altered form. The historical perspective which comes from such a study cultivates a wholesome scepticism about many current details, but it also encourages one to believe that there is some central truth which will persist. It should also help us to realize how fragmentary and incomplete our knowledge about the most fundamental problems of chemistry still is.

Valence, at its basis, is a theory about how atoms combine. Without the aid of the atomic theory, Lavoisier suggested, for acids, bases and salts, that elements combine in pairs, the base being a compound of a metal with oxygen, the acid a compound of a non-metal with oxygen, and the salt a binary compound of a second order, between an acid and a base. This dualistic character of chemical combination seems to us, today, even more fundamental than Lavoisier suspected.

After Dalton had discovered that chemical combination takes place between atoms, and Davy had made his brilliant discoveries of potassium and sodium by the decomposition of caustic potash and caustic soda with the electric current,

it was very natural that Davy and Berzelius should suppose that atoms have positive or negative charges and that the attraction which holds atoms together in compounds is due to the attraction between these charges. Metals were supposed to be positive, non-metals negative, and oxygen intermediate between the two. In salts, bases were thought to be positive and acids negative. These ideas are illustrated by the following formula:

$$\begin{array}{ccccc} & + & & - & \\ + & - & & - & + \\ Ca & O & \cdot & S & O_3 \end{array}$$

Faraday's Law. Thirty years later Faraday showed that if an electric current is passed through a series of solutions of electrolytes, the quantities of the ions which separate are proportional to the combining weights of the elements.

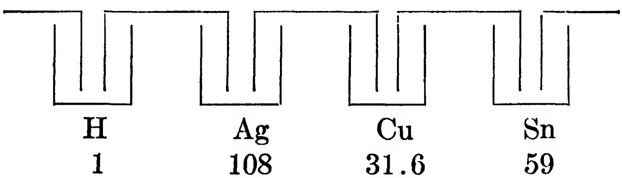


FIG. 9. Faraday's law.

It is evident from Faraday's law that if chemical elements consist of atoms there must be one or more atoms of electricity associated with each atom. Faraday does not seem to have drawn this obvious conclusion and it was fifty years later when Helmholtz, in his Faraday lecture before the Chemical Society in London, first used the expression, "atom of electricity." He could have had, at that time, only a very vague idea of the real meaning of the expression. It was long after that before physics began to think in terms of electrons.

Substitution. Soon after the discovery of Faraday's law, Dumas discovered trichloroacetic acid. He showed that this is a monobasic acid and decomposes to chloroform and car-

on dioxide very much as acetic acid decomposes to meth-
ne and carbon dioxide:

$$CCl_3 \; \underline{|CO_2|} \; H \qquad\qquad CH_3 \; \underline{|CO_2|} \; H$$

The chemists of that day considered hydrogen as positive nd chlorine as negative. It seemed to them impossible that ne could be substituted for the other without a complete hange in the character of the compound. To express this iew, Wöhler, a pupil and ardent follower of Berzelius and f his electrochemical theory, published a brilliant satire in rench, in Liebig's *Annalen*. He signed it S. C. H. Windler.* t purported to be an account of some experiments carried ut by treating manganese acetate with chlorine. According o the article, the manganese was replaced by the chlorine, hen the hydrogen, the oxygen and the carbon. The compound prepared in this way was claimed to have the same eneral properties as the manganese acetate—but Windler dmitted that it smelled like chlorine hydrate!

At that time, the old electrochemical theory had been aining favor steadily for 30 years and Wöhler undoubtedly xpressed the common opinion of the chemists of his day, ut the facts soon accumulated in support of the theory of ubstitution, compelled the abandonment of the electrochemical theory and a return to Dalton's idea of an attraction between the atoms as the cause of chemical combination. During the last half of the nineteenth century a large majority of the chemists of the world were busy deciphering the structure of organic compounds and preparing tens f thousands of new ones. While the terms "positive" and negative" groups were frequently used, the meaning attached to the words had no definite relation to electrical properties. Practically, Dalton's simple idea of an attraction between the atoms was assumed as the cause of chemical combination.

* It seems hardly necessary to suggest that this may be written chwindler.

Chains of Atoms. Frankland added, however, a new and very fundamental concept when he suggested that an atom can hold, directly, to only a small number of other atoms and that the numbers which can be held in combination vary for different atoms. Couper and Kekulé added the further idea that carbon atoms, especially, may form chains and rings in an endless variety of forms. LeBel, van't Hoff and Baeyer showed that the attractions hold the atoms combined with a quadrivalent element in such a geometrical relation that they do not readily exchange places. Couper and Kekulé assumed only a sequence of atoms but the phenomena of optical activity, of doubly united carbon atoms and of rings, compelled the consideration of relations in three dimensions.

During the last half of the nineteenth century a number of brilliant discoveries were made, which can now be seen as related to the problem of the nature of the forces which hold atoms together. In most cases, the discoverers had very little appreciation of these relations.

II. Modern Electrochemistry

Ionization. In 1859 Hittorf discovered the independent migration of the ions of an electrolyte. Under the influence of an electric current, hydrogen ions travel toward the cathode four times as fast as chloride ions travel toward the anode. It was nearly 30 years later when Arrhenius proposed his hypothesis of ionization and gave a clear explanation for Hittorf's experiments. This started a new electrochemistry as applied to electrolytes. Beginning with Raoult's laws for the relation between the freezing points and boiling points of solutions and the molecular weights of solutes, and the work of van't Hoff on the thermodynamics of solutions, it was soon found that the ions in a solution obey Avogadro's law, subject to limitations somewhat similar to those we meet when the law is applied to the conduct of easily condensible gases. The modern theory that atoms consist of a

central nucleus having a positive charge which is balanced by the negative charges of the electrons surrounding it, has thrown further light on the independence of ions in solution and of molecules in a gas. In a gas, the molecules are electrically neutral and have no electrical attraction or repulsion for each other, except that, when close together, the repulsion of the electrons in their outer shells cause them to fly apart. The charges on the ions cause them to approach each other and cause the number of ions of opposite sign in any part of a solution to remain equal, but the electrons in the shells of the ions force them apart when they come close together.

Cathode Rays. In the late 70s, Crookes discovered the cathode rays. It was twenty years later when J. J. Thomson demonstrated that these rays are composed of electrons, atoms of negative electricity, and determined their electrical mass, 1800 times less than that of hydrogen atoms. Crookes had shown the material character of the rays by causing them to impinge on the vanes of a small wheel, which rotated when the electrons struck on one side of the vanes. He also showed their character as negative electrical particles by deflecting the cathode stream with a magnet.

Crookes's discovery was important, not only in its relation to electrons, but from it came, in logical sequence, Röntgen or x-rays, Becquerel rays, radium, disintegration of atoms, isotopes, Moseley's atomic numbers and modern theories of the structure of atoms.

Arrhenius's theory of ionization, while it was a new and very important electrochemical theory and opened up a very fertile field for experimental investigation, raised more questions about the nature of chemical combination than it solved. The ions are evidently charged bodies. How do they acquire their charges? Do the charges persist and hold the ions together in the un-ionized compounds? If they do hold the ions together in the un-ionized compounds, why can the ions separate so easily and remain apart in solution? The

new ideas of atomic structure are giving a partial answer to these questions, which were scarcely asked during the first twenty years of the new physical (so-called "allgemeinen" or "general") chemistry.

Positive-negative Theory. Van't Hoff in 1895 first used the ionic idea to explain a reaction involving substances which are not electrolytes, when he was considering the formation of ozone in the presence of moist phosphorus. He never returned to the subject but many others must have had similar ideas. In 1901, Noyes and Lyons in studying the action of chlorine on ammonia, proposed an ionic explanation of the results, assuming, especially, that molecular chlorine, Cl_2, separates into positive and negative ions, Cl^+ and Cl^-. Some of the suppositions in their paper now seem quite wrong. Stieglitz had previously given an ionic explanation of the reaction between chlorine and water but had not published his ideas, except orally in the class room.

$$Cl^+ + Cl^- + OH^- + H^+ = ClOH + Cl^- + H^+$$

Lapworth, in England, expressed similar ideas. None of these papers led, at the time, to further experimental work or had any immediate effect toward the development of a theory of positive and negative valences.

III. Electronic Theory

J. J. Thomson. Quite independently, J. J. Thomson, in 1903, proposed the first electronic hypothesis about the structure of atoms and the function of electrons in chemical combination. He suggested that an atom might consist of a sphere of positive electricity within which electrons arranged themselves in accordance with the attraction of the sphere, drawing them to the center, and the mutual repulsion between the electrons. By the transfer of an electron from one atom to another, the atom losing the electron would become positive and the other would become negative. This accounts satisfactorily for the formation of ions

and that part of the theory is still accepted. The hypothesis is not so good in explaining compounds which are not electrolytes but it became the incentive to the development of the positive-negative theory by Falk and Nelson, Stieglitz, L. W. Jones, Fry, Noyes, and others.

Rutherford.—Heavy Nucleus. Rutherford's study of the scattering of alpha particles which pass through an atom close to the nucleus, together with Bohr's theory of the structure of atoms and the origin of spectral lines, caused the abandonment of Thomson's hypothesis of a diffuse sphere of positive electricity with electrons inside, and demonstrated that the electrically positive portion of the atom, carrying about 99.97 per cent of the mass, is concentrated very close to the center of the atom.

The discovery of the Becquerel rays, the isolation of radium by the Curies, the theory of atomic disintegration of Rutherford, the demonstration by Rutherford, Ramsay and Soddy that helium is formed by the disintegration of radium, and the discovery by Rutherford and others that hydrogen and an isotope of oxygen are formed by the bombardment of nitrogen atoms with alpha particles, have convinced chemists and physicists that atoms are not the indivisible, unchanging and unchangeable particles they were once thought to be.

Fundamental Concepts. The modern theories of the structure of atoms have been discussed in the preceding chapters and the discussion need not be repeated. The elements of these theories of most interest to the chemist in considering the phenomena of chemical combination are:

The probably indivisible character of electrons and protons and the indivisibility of the nuclei of atoms in ordinary chemical changes; the unit negative charge of an electron exactly balanced by the unit positive charge of a proton; the attraction between electrons and protons or positive nuclei; the repulsion of electrons for electrons and of protons for protons; and the identity between the number

of electrons in the shell of a neutral atom and the number of unit positive charges in the nucleus, both being equal to the atomic number of the element.

The new forms of atom mechanics and the recognition of the wave-like properties of electrons and protons have not, as yet, interfered with these fundamental concepts. Physicists have become much more cautious than Bohr was, however, in assigning definite locations for the orbits and positions of the electrons. In general, they try to avoid pictures in three-dimensional space. For chemical purposes such pictures are, at present, useful. They should, however, be employed cautiously and considered carefully to discover their limitations.

IV. Theory of G. N. Lewis

Soon after the determination of the mass of an electron by J. J. Thomson and the identification of Crookes's cathode rays as streams of electrons, G. N. Lewis began the consideration of an electronic theory of valence. He spoke of the subject from time to time in his classes but did not publish his theory till 1916. About the same time as the publication of Lewis's paper, Kossel, in Germany, emphasized the importance of a shell of eight electrons as a basis for a theory of chemical combination.

In 1919, Irving Langmuir, in a series of brilliant addresses, called attention to Lewis's theory and developed it further. The most essential parts of the theory are as follows:

1. Shells of Electrons. The electrons surrounding the nuclei of atoms may be considered as arranged in shells which may be represented, diagrammatically, in Fig. 10, for the first two periods of the elements.

The nucleus together with the electrons of the inner shell or shells, form the *kernel* of each atom. This is enclosed with a circle in the diagrams. The dots outside of the circles represent the valence electrons. These are usually the only

electrons concerned in chemical combination. There are very probably exceptions to this, especially for elements having several shells of electrons and possibly for boron. The kernels of the atoms of the first period contain two electrons; those of the second period, ten. The numbers to the right of each symbol give the positive kernel charge and also the atomic number.

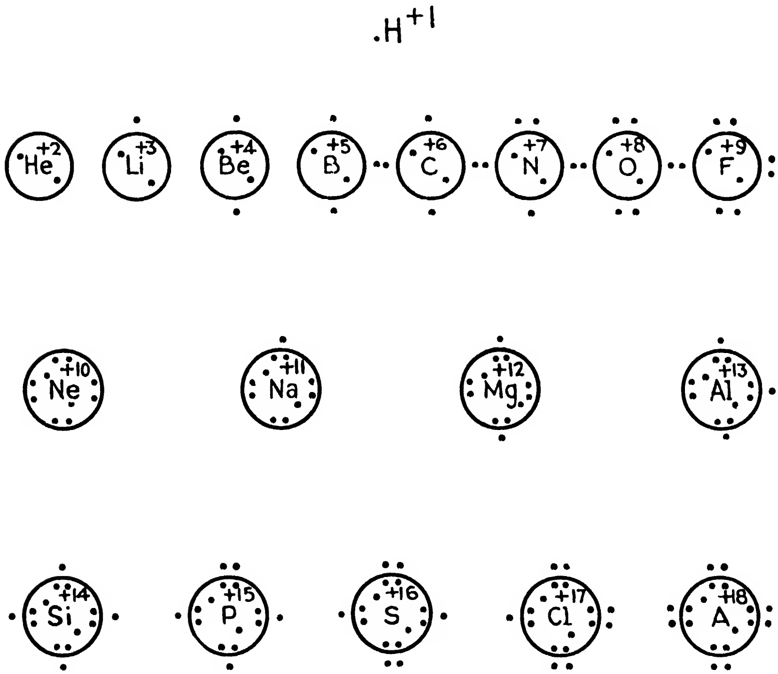


Fig. 10. Diagrammatic representation of the electronic structure of isolated, electrically neutral atoms.

2. **Octets.** There is a strong tendency for atoms to revert to an arrangement of their electrons corresponding to a molecule (atom) of a noble gas with two or eight electrons in the outer shell—helium, neon and argon in the diagram. As the elements of the first period have only two electrons in their kernels, lithium and beryllium retain only this kernel in

their normal reactions, though there seems some possibility that the two electrons of the kernel are involved in some cases. Boron is anomalous and possibly forms a shell of six electrons in some cases. Nitrogen seems to have a shell of seven electrons in nitric oxide and nitrogen dioxide.

3. Pairs of Electrons. In nearly all cases, electrons go in pairs. The alkali metals and chlorine, bromine, and iodine have odd electrons at high temperatures, hydrogen may be prepared with an odd electron, but other cases are rare and compounds with odd electrons are usually very reactive.

The various methods of securing an octet for the outer shell of an atom and the conduct of pairs of electrons will be discussed in the following pages.* In doing this a fourth principle, not clearly recognized by Lewis and Langmuir, is freely used.

4. Sextets. In nearly all reactions occurring at ordinary temperatures, when two atoms held together by a covalence separate, the pair of electrons of the covalence remains with one of the atoms, causing that atom to be, temporarily, negative and the atom from which it separates, positive. The positive atom has only six electrons and that ion has only an ephemeral existence.

* In what follows, an attempt is made to develop a logical, consistent, electronic theory of valence for the elements from hydrogen to calcium, inclusive, taking into consideration: the older, positive-negative views of Arrhenius, van't Hoff, W. A. Noyes and Lyons, Stieglitz, J. J. Thomson, Falk and Nelson, Fry, L. W. Jones and others; the theories of the structure of atoms of Rutherford, Bohr, Sommerfeld, McLellan and, to some extent, the new wave mechanics; the theory of octets and shared electrons of G. N. Lewis, Kossel and Irving Langmuir; the theory that a pair of electrons may be drawn more strongly toward one or the other of a pair of atoms held together by a covalence, of G. N. Lewis, Langmuir, Stieglitz, W. A. Noyes and others; the theory of inclusive orbits of W. A. Noyes, C. A. Knorr, N. R. Campbell, Nicholson, Sidgwick, Pauling, Glockler and Sommerfeld; the nature of the chemical bond developed in terms of the quantum mechanics by Heitler, London, Linus Pauling and Mulliken; and the double and triple covalences and mixed or semipolar valences of Lowry, of Harrison, Kenyon and Phillips, of Sugden and of W. A. Noyes. Such a list can hardly fail to have some important omissions.

Positive Polar Valences are formed by the loss of the valence electron or electrons. This gives a positive ion because the charge of the nucleus is no longer balanced by the electrons of the kernel which remains. Lithium, sodium and potassium give univalent ions by the loss of a single electron; beryllium, magnesium and calcium give bivalent ions by the loss of two electrons. Such ions, because of their noble gas structure, cannot share electrons with other atoms (see Covalences, below) and they maintain a quasi independent existence in solutions and even in crystals. The latter is shown by the x-ray examination of sodium chloride and other compounds. The static attraction between atoms of sodium and chlorine will, however, hold them together in pairs in the gaseous state and will cause all parts of a solution to remain electrically neutral, if the parts are large enough to include a number of molecules.

The static attraction between ions which form parts of a molecule may also hold the molecule in a stable configuration, as in aminolauronic acid, $C_8H_{14}\langle{}^{CO}_{NH_3}\rangle O$, in which the static attraction of the negative oxygen of the acid ion for the positive nitrogen of the ammonium ion holds the molecule together as a ring in an aqueous solution.

Hydrogen ions are positive ions of a very unique character because they have no shell of electrons. They may, therefore, easily enter into covalences or come close to atoms or ions which cannot share their electrons. This gives a simple explanation for the fact that many acids are only slightly ionized in solutions, while their sodium or potassium salts are highly ionized. It may give a partial explanation for water of hydration.

Negative Polar Valences are formed by the gain of an electron, giving an ion in which the electrons of the shell overbalance the charge of the nucleus. A chlorine atom takes up an additional electron to form a chloride ion,

$:\!:\!:\overset{::\,-}{\underset{::}{Cl}}:\!:$, which has a negative charge because there are 18 electrons in its shell, while the nucleus of the chlorine atom has only 17 units of positive charge. The ion has a quasi independent existence in solutions and in crystals because of its noble gas structure.

Covalences are formed when two atoms share a pair of electrons. Each atom completes its octet in this manner and the pair of electrons performs, for each atom, the function of a single electron in balancing the charge of the nucleus of the atoms.

Rule for the Sum of the Covalences and of the Unshared Electrons. It has been pointed out, on the basis of the disintegration of radioactive elements, that in every neutral atom the number of electrons in the shell must exactly equal the number of units of positive charge in the nucleus. When ions are formed by the gain or loss of electrons, every positive ion must have a negative ion in the immediate neighborhood, and in the gaseous state positive and negative ions may be held together by their static attraction for each other. Such considerations lead to the simple rule:

In any compound having only covalences the number of covalences plus the number of unshared electrons, for each atom, will equal the number of valence electrons for that atom. The application of the rule will be apparent from the following electronic formulae, in some of which double and triple covalences are assumed (see semipolar unions and double covalences, p. 108). The electrons of the kernels are not represented in these formulae.

$$H:H \quad :N:::N: \quad \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}::\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} \quad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: \quad H:\overset{H}{\overset{\cdot\cdot}{\underset{\underset{H}{\cdot\cdot}}{C}}}:H \quad H:\overset{H}{\overset{\cdot\cdot}{\underset{\underset{H}{\cdot\cdot}}{N}}}:$$

$$H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H \quad H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H \quad :\overset{\cdot\cdot}{O}::C::\overset{\cdot\cdot}{O}: \quad \cdot\overset{\cdot\cdot}{N}::\overset{\cdot\cdot}{O}: \quad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:\overset{\cdot\cdot}{N}::\overset{\cdot\cdot}{O}:$$

These formulae and the formulae given under semipolar unions p. 108 give a very satisfactory explanation of the principal and contra valences of Abegg and of some of the variable valences which caused chemists so much trouble sixty or seventy years ago.

Complex Ions. The rule given in the last paragraph furnishes a logical explanation for the formation of complex ions. Just as the completion of an octet by the gain or loss of an electron gives an ion consisting of a single atom, the completion of an octet by means of a covalence may leave the kernel charge of the atom overbalanced or underbalanced. The hydroxyl group $\mathrm{H}:\overset{\cdot\cdot\;-}{\underset{\cdot\cdot}{\mathrm{O}}}:$, is negative because the sum of the unshared electrons, plus the covalence, is seven for the oxygen atom, while oxygen has only six valence electrons. The ammonium group $\begin{array}{c}\mathrm{H}\\ \mathrm{H}:\overset{\cdot\cdot\;+}{\underset{\cdot\cdot}{\mathrm{N}}}:\mathrm{H}\\ \mathrm{H}\end{array}$, is positive because the nitrogen atom of the group has only four covalences and the five positive charges of the nitrogen kernel are underbalanced. The phenyliodonium group, $\mathrm{C^6H^5}:\overset{\cdot\cdot\;+}{\underset{\cdot\cdot}{\mathrm{I}}}:\mathrm{C^6H^5}$, is positive because the sum of the covalences and unshared electrons is six for the iodine, while iodine has seven valence electrons.

The conduct of the ammonium group deserves a little further consideration. Both pure water and pure ammonia undergo a trifling ionization to hydrogen ions, $\mathrm{H^+}$, and negative hydroxide, $\mathrm{H}:\overset{\cdot\cdot\;-}{\underset{\cdot\cdot}{\mathrm{O}}}:$ or amide, $\begin{array}{c}\mathrm{H}\\ \mathrm{H}:\overset{\cdot\cdot\;-}{\underset{\cdot\cdot}{\mathrm{N}}}:\end{array}$, ions. The ammonium group, $\begin{array}{c}\mathrm{H}\\ \mathrm{H}:\overset{\cdot\cdot\;+}{\underset{\cdot\cdot}{\mathrm{N}}}:\mathrm{H}\\ \mathrm{H}\end{array}$, probably shares the tendency of ammonia to give up hydrogen ions, in an enhanced degree, and the group can exist in large numbers only in the pres-

ence of hydrogen ions. In a solution of ammonia in water, the equilibrium,

$$H:\overset{\overset{\textstyle H}{..}}{\underset{\underset{\textstyle H}{..}}{N}}{}^{+}:H+:\overset{..}{\underset{..}{O}}{}^{-}:H\rightleftarrows H:\overset{\overset{\textstyle H}{..}}{\underset{\underset{\textstyle H}{..}}{N}}:+H:\overset{..}{\underset{..}{O}}:H,$$

causes the ammonia to exist almost entirely as free ammonia. Very few ammonium and hydroxide ions are present.

Even when an acid with a low ionization constant, such as acetic acid, is present, the equilibrium, $NH_4^+ + CH_3CO_2^- \rightleftarrows NH_3 + CH_3CO_2H$, will cause the formation of so much free ammonia that this escapes rapidly on distillation. This conduct of solutions of ammonium acetate is, of course, well known.

Even a neutral solution of ammonium chloride becomes faintly acid on distillation in accordance with the equilibrium, $NH_4^+ + Cl^- \rightleftarrows NH_3 + Cl^- + H^+$. The increase in the number of hydrogen ions, however, soon reduces the number of molecules of ammonia to a negligible amount. But we may assume that even in the presence of a large number of hydrogen ions there are some molecules of free ammonia present, just as we assume that some hydroxide ions are present in a strongly acid solution.

The conduct of sulfur hexafluoride makes it seem probable that there are six covalences in this compound.

$$\begin{array}{ccc} & F & \\ F: & .. & :F \\ & S & \\ F: & .. & :F \\ & F & \end{array}$$

Such a formula agrees with the rule for covalences but requires the assumption of a shell of 12 electrons about the sulfur kernel.

A similar structure would account for the fluosilicate ion.

```
       F =
F:  ··  :F
       Si
F:  ··  :F
       F
```

Because there are six covalences while silicon has only four valence electrons, the silicon atom has an excess of two negative charges and the group SiF_6 is a complex negative ion. Such considerations, however, would carry us over to the consideration of atoms with more complex ionic shells. These do not fall within the scope of this chapter.

Theory of Inclusive Orbits. In his theory as at first proposed, Lewis assumed electrons in a condition of static equilibrium between two atoms held together by a covalence. Such a supposition is not easily reconciled with the theories of the structure of atoms nor with the velocities of electrons when they escape from an atom. Bohr suggested that an electron may rotate in an orbit at right angles with the line joining the nuclei of two atoms, but that hypothesis has not proved satisfactory.

In 1917, W. A. Noyes suggested that two atoms might be held together by an electron revolving in an orbit which included two positive nuclei. The hypothesis was very crude and did not take account of the concentration of the positive charge of an atom in a single nucleus or of the fact that a covalence seems to involve two electrons. Quite independently, the theory of inclusive orbits was proposed by N. R. Campbell, Nicholson and Sidgwick in England and by C. A. Knorr in Germany. The structure of methane supposed by Knorr is shown in Fig. 11.

This theory has been considered favorably by Pauling, Glockler, Sommerfeld and others and has been made the basis for extensive discussions of valence by Sidgwick and by Robert Müller. It has been used by W. A. Noyes to explain the magnetic character of hydrogen atoms and the non-magnetic character of hydrogen molecules.

A theory of shared electrons based on the quantum mechanics and somewhat related to the older theory of inclusive orbits, has been referred to (p. 71). Fig. 12 shows a

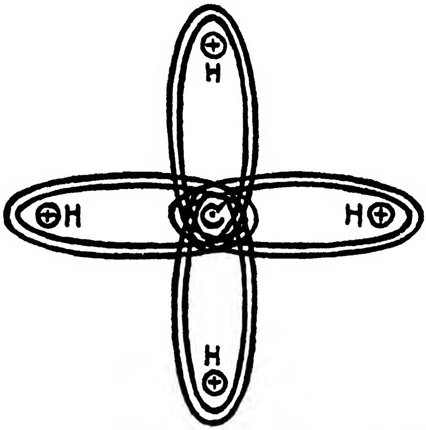


FIG. 11. Inclusive electronic orbits of methane, after Knorr. (From *Zeitschrift für Anorganischen Chemie.*)

diagrammatic interpretation of the direction of the bonds of a carbon atom as given by Linus Pauling and Fig. 13 gives his interpretation of a double bond between two car-

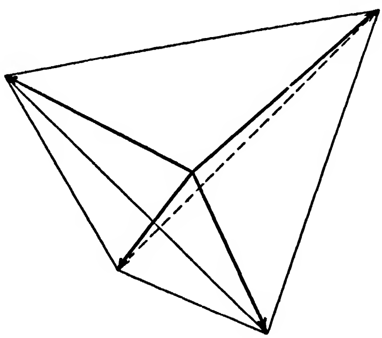


FIG. 12. Quantum mechanics interpretation of the carbon bonds, by Linus Pauling. (From the *Journal of the American Chemical Society.*)

bon atoms, which does not permit free rotation about the line joining their nuclei.

Potential Polar Valences. The positive-negative theory

of covalences, involving the idea of the transfer of an electron from one atom to the other and an electrostatic force holding the atoms together, was supported during the first fifteen years of the twentieth century, by the fact that many atoms held together by covalences react in such a manner as to indicate that one of them is positive and the other negative. Methyl iodide, CH_3I, when it reacts with water

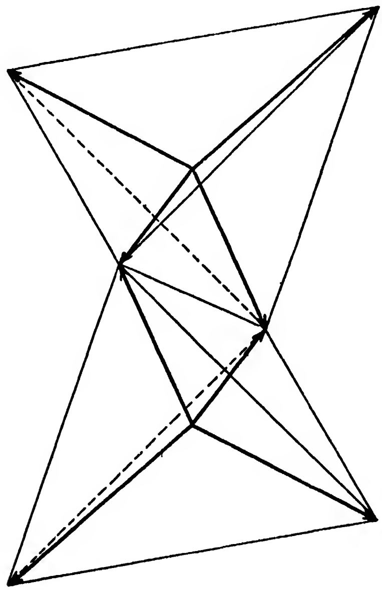


FIG. 13. Quantum mechanics interpretation of a double union between carbon atoms by Linus Pauling. (From the *Journal of the American Chemical Society*.)

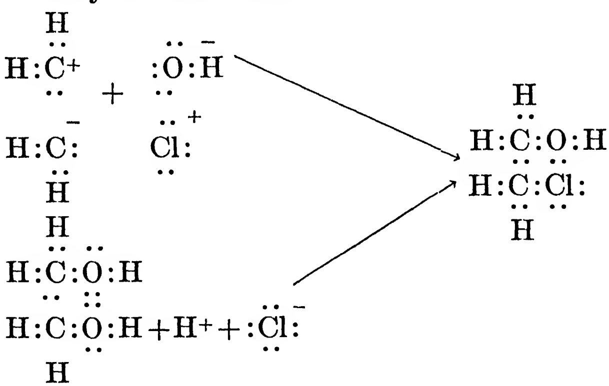
gives the iodide ion and methyl alcohol, CH_3OH. Ammonia reacts with chlorine, Cl_2, forming the chloroammonium ion, NH_3Cl^+, which immediately loses a hydrogen ion, H^+, to balance the chloride ion, Cl^-, left by the separation of the chlorine molecule into positive and negative chlorine.

The bromide ion, Br^-, adds to the second carbon atom of butene and the hydrogen ion to the end, indicating the intermediate formation of the electronic grouping,

$$\begin{array}{ccccccc} & H & & H & & & \\ & .. & & .. & & \overset{+}{} & ..\,- \\ H: & C & : & C & :C: & & C:H, \\ & .. & & .. & .. & & .. \\ & H & & H & H & & H \end{array}$$

in which the end carbon atom is negative and the second, positive. Nitrogen trichloride adds the negative ion, $\overset{\displaystyle Cl}{\underset{..}{\overset{..\,-}{Cl:N:}}}$, to the second carbon atom and the positive chloride ion, $\underset{..}{\overset{..\,+}{:Cl}}$, to the end, giving the compound, CH_3 $CH_2CHNCl_2CH_2Cl$.

The failure to obtain an electromer of nitrogen trichloride in which the chlorine would react in the negative form, $\overset{\displaystyle Cl}{\underset{..}{\overset{..\,+}{Cl:N}}} + \underset{..}{\overset{..\,-}{:Cl:}}$, and the fact that the chlorohydrin formed by the addition of hypochlorous acid to ethylene is identical with that formed by the replacement of the hydroxyl of glycol by the chloride ion, furnish almost conclusive evidence that the pair of electrons forming a covalence is held in common by the two atoms.



These facts are easily explained by the covalence theory with the aid of the assumption that the atoms united by a covalence usually separate in such a manner that the pair of electrons remains with one of the atoms, leaving the atom from which the electrons are removed, positive. In

other words, the atoms united by a covalence are often *potentially* positive and negative. It seems better to reserve the words positive and negative, when used without the qualifying adjective, for atoms or groups which are actually ions, either the ions of solutions, the ions temporarily formed in a chemical reaction, or the ions of semipolar unions.

The reason for potential polarity may usually be explained by the character of the kernels of the atoms or by the character of neighboring atoms in the molecule. The chlorine atom has a kernel of seven positive unit charges and in separating from carbon, which has a kernel charge of four, it will usually retain the pair of electrons and react as a chloride ion. In nitrogen trichloride, the kernel of the nitrogen atom has only two electrons while that of the chlorine atom has ten. Although the kernel charge of the nitrogen is only five while that of the chlorine is seven, the closer proximity of the nucleus causes the electrons to remain with the nitrogen when the atoms separate.

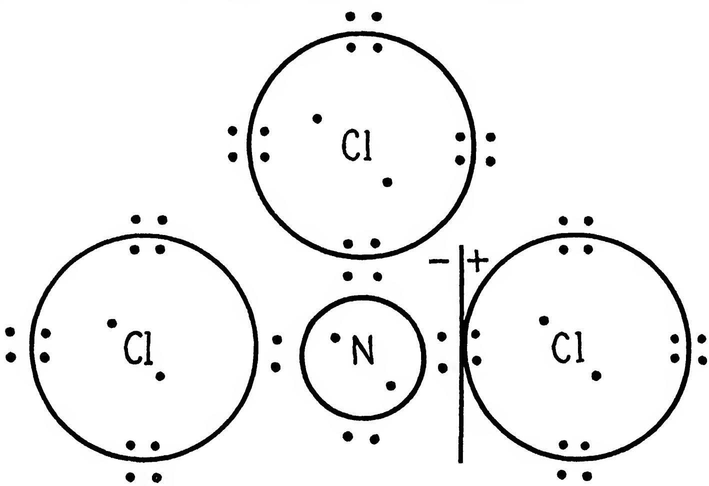


Fig. 14. Diagrammatic representation of the ionization of nitrogen trichloride in reactions.

In phosphorus trichloride, however, both atoms have ten electrons in their kernels and the chlorine with its kernel

charge of seven takes the electrons away from the phosphorus with its kernel charge of five.

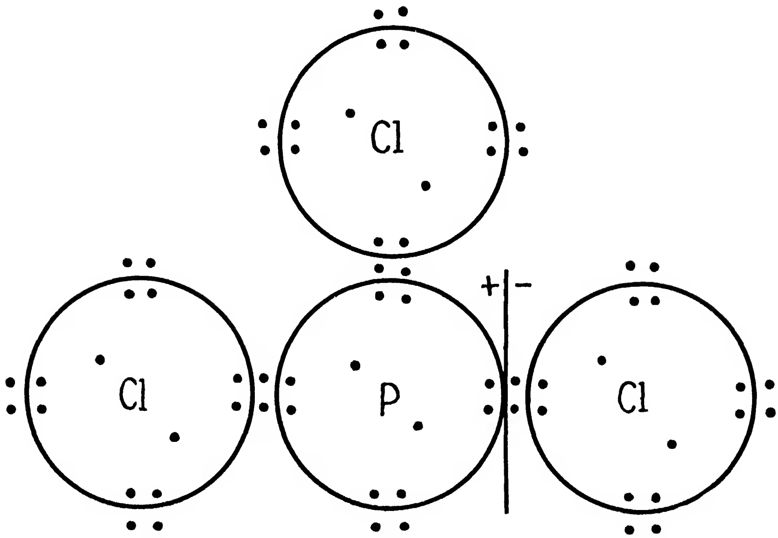


FIG. 15. Diagrammatic representation of the ionization of phosphorus trichloride in reactions.

The effect of such atoms as oxygen and chlorine, with large kernel charges, on neighboring atoms in the molecule is seen, especially, in the ionization constants of acids and in the Kolbe, Reimer-Tiemann, Perkin and other condensation reactions, where a hydrogen atom attached to a carbon atom adjacent to another carbon atom which is combined with oxygen, readily separates from the carbon in the ionic form.

Semipolar Unions and Double Covalences. More than fifty years ago, van't Hoff suggested that a double union between carbon atoms may hold the atoms in such a manner that there is no free rotation about the point of union, while free rotation is possible for a single union. No optical activity has been observed as due to a carbon atom which is doubly united to another carbon atom.

Harrison, Kenyon and Phillips have found a number of

sulfur compounds of the type,

$$\begin{array}{ccccc} & & \cdot\cdot & & \\ R & : & S & : & R \\ & & \cdot\cdot & {}^{+} & \\ & : & O & : & \\ & & \cdot\cdot & {}_{-} & \end{array}$$

which are optically active and in which the sulfur atom is the only one which can be asymmetric. They think the asymmetry is due to a semipolar union between the sulfur and the oxygen and to the two free electrons which complete the tetrahedral arrangement necessary for the asymmetry of a single atom. It will be seen that according to the rule for covalences and shared electrons, the sulfur atom is positive and the oxygen negative. The two are held, therefore, by one covalence and one polar union. Such a union was called a mixed double bond by Lowry but, more appropriately, a semipolar bond, by Sugden.

This hypothesis has received very welcome support by the determination of the "parachor" of the compounds by Sugden. Eighty years ago Kopp showed that by determining the densities of substances at their boiling points and dividing the molecular weights by the densities, values for molecular volumes were obtained which were much more consistent with the atomic volumes he assumed than when the densities were determined at ordinary temperatures. His idea seems to have been that when the molecules are ready to separate from each other and assume the gaseous state, the volumes filled by the molecules are free from external relations. He was probably not aware that at the boiling point there is still a large internal pressure due to the attraction of the molecules for each other. At the critical temperature of a liquid, this internal pressure disappears. Sugden has found a function related to the critical temperature which he combines with the density to calculate what he calls the "parachor." This parachor, as he has shown, is dependent partly on the parachors of the atoms of which the compound is composed and partly on the structure of the compound. For compounds for which

we have good reasons for assuming double or triple unions or rings of three or four atoms, there are considerable increases for the parachor above the sum of the parachors of the atoms. For the compounds of Harrison, Kenyon and Phillips and for derivatives of sulfuric acid, in which Lewis and Langmuir have assumed single covalences, the parachors are quite close to the sums of the parachors of the elements. The parachors of nitro compounds and of nitric esters indicate one double bond and one semipolar bond between nitrogen and the oxygen atoms. There can be little doubt that the structures of sulfuric, nitric and perchloric acids are:

$$
\begin{array}{c}
:\!O\!: \\
\cdot\cdot\ \ \cdot\cdot\ {}^{+}\ \cdot\cdot - \\
H\!:\!O\!:\!N\!:\!O\!: \\
\cdot\cdot\qquad\ \ \cdot\cdot
\end{array}
\qquad
\begin{array}{c}
\cdot\cdot - \\
:\!O\!: \\
\cdot\cdot\ \ \cdot\cdot+\cdot\cdot \\
H\!:\!O\!:\ S\ :\!O\!:\!H \\
\cdot\cdot\ \ \cdot\cdot+\cdot\cdot \\
:\!O\!: \\
\cdot\cdot -
\end{array}
\qquad
\begin{array}{c}
\cdot\cdot - \\
:\!O\!: \\
\cdot\cdot+\ \cdot\cdot+\cdot\cdot - \\
H\!:\!O\!:\!Cl\!:\!O\!: \\
\cdot\cdot\ \ \cdot\cdot+\cdot\cdot \\
:\!O\!: \\
\cdot\cdot -
\end{array}
$$

These formulae furnish a practically complete reconciliation of the Lewis and Langmuir formulae with the principles of shared and unshared electrons. They also show how the valence of chlorine varies from one to seven and that oxygen is bivalent in all its ordinary compounds.

The conversion of trimethylamine to trimethylamine oxide furnishes an excellent illustration of a number of the principles of electronic valences. Hydrogen peroxide separates into positive and negative hydroxyl groups as molecular chlorine separates into positive and negative chlorine ions, $H\!:\!\overset{\cdot\cdot\,-}{\underset{\cdot\cdot}{O}}\!:\quad {}^{+}\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}\!:\!H$. The positive hydroxyl can unite with the unshared electrons of the trimethylamine, giving the trimethylhydroxy-ammonium ion, $\begin{array}{c} CH_3{}_{+} \\ CH_3\!:\!\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}\!:\!\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}\!:\!H, \\ CH_3 \end{array}$ which is positive because the nitrogen has four covalences,

as in the ammonium ion. Such an ion will lose a hydrogen ion to a hydroxyl group in an alkaline solution, leaving trimethylamine oxide, $\begin{matrix} & CH_3 & \\ CH_3: & \overset{\cdot\cdot+}{\underset{\cdot\cdot}{N}}: & \overset{\cdot\cdot-}{\underset{\cdot\cdot}{O}}: \\ & CH_3 & \end{matrix}$, with a semipolar union between the oxygen and nitrogen atoms. That it does this is demonstrated by the excessively low conductivity of a solution of trimethylamine oxide and the high conductivity of trimethylhydroxyammonium bromide, formed when hydrobromic acid is added to a solution of the oxide. The addition of the hydrobromic acid gives the ion, $\begin{matrix} & CH_3{}^{+} & & \\ CH_3: & \overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}: & \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}: & H \\ & CH_3 & & \end{matrix}$ and Br^-, very much as hydrochloric acid gives with ammonia, ammonium ions and chloride ions.

Oxidation and Reduction have been defined as the loss or gain of electrons, according to the older positive-negative theory. A consideration of electronic mechanisms in the light of the discussions of this chapter leads us to distinguish three types of oxidation.

1. Transfer of an Electron. When sodium is oxidized by chlorine, two electrons of sodium atoms are transferred to a molecule of chlorine, giving two sodium and two chloride ions. When sodium dissolves in water, each sodium atom gives its electron to a hydrogen ion. The hydrogen ions are reduced to free hydrogen. The hydrogen ion, not water, is the oxidizing agent:

$$2Na' + 2H^+ + 2:\overset{-\,\cdot\cdot}{\underset{\cdot\cdot}{O}}:H = 2Na^+ + H:H + 2:\overset{-\,\cdot\cdot}{\underset{\cdot\cdot}{O}}:H$$

When aluminum dissolves in a solution of sodium hydroxide, there is a similar exchange of electrons between the aluminum and the hydrogen ions of the solution, though the latter are present in small numbers. The fact that the hydroxyl ions unite with the aluminum with a covalence, giving an amphoteric hydroxide and reducing the hydroxyl

ion concentration, is probably an important factor in the phenomenon.

The oxidation of *o*- or *p*-cresol, with evolution of hydrogen, when they are fused with potassium hydroxide, is best explained in a similar manner. The semipolar oxygen of the cresylate ion, $CH_3C_6H_4:\overset{\cdot\cdot\,-}{\underset{\cdot\cdot}{O}}:$, enhances the tendency of the hydrogen atoms in the methyl group in the ortho or para position to assume the ionic form, as hydrogen atoms in the ortho or para position do in the Kolbe and Reimer-Tiemann syntheses. The hydrogen atoms, in this case, do not escape in the ionic form, however, but take electrons from the carbon atom of the methyl group and escape as free hydrogen, each hydrogen atom uniting with a hydrogen ion from the water. This leaves the carbon atom without electrons and prepared to unite with hydroxyl ions. This gives the group,

$$\begin{array}{l} \quad :\overset{\cdot\cdot}{O}:H \\ C:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H \\ \quad :\underset{\cdot\cdot}{O}:H \end{array}$$

which loses water, as usual, giving the carboxyl group.

2. Oxidation by Positive Hydroxyl. The explanation of the oxidation of trimethylamine to trimethylamine oxide has been given and need not be repeated here. A somewhat similar explanation seems to be the most satisfactory for the autoxidation of hypochlorous acid to chloric acid. This occurs most easily in a faintly acid solution.

Some years ago, a consideration of the formation of hypochlorous acid by the addition of the hydroxyl of water to the positive chlorine from a molecule of free chlorine, suggested the possibility that hypochlorous acid may be amphoteric, ionizing to hydroxyl and positive chlorine, as well as to hydrogen and hypochlorite ions. A new method was devised by Wilson, which gave an accurate ionization constant for hypochlorous acid and for a solution of sodium hypochlorite. This showed that the constant is very low

and is due to hydrogen and hypochlorite ions. An attempt to show hydroxyl ionization by determining the conductivity of a solution of hypochlorous acid to which a little nitric acid was added, failed because of the very slight ionization in this direction. That such an ionization occurs was shown, however, by a method suggested by an observation of Balard, made nearly a century ago. He found that chlorine monoxide is formed when a solution of hypochlorous acid is treated with anhydrous calcium nitrate. By means of appropriate experiments, Noyes and Wilson demonstrated that chlorine monoxide is found in the gaseous phase above a solution of hypochlorous acid. The only simple explanation is that this is formed by the amphoteric ionization of the hypochlorous acid: $\begin{matrix} H^+ & ClO^- \\ HO^- & Cl^+ \end{matrix}$. A solution of hypochlorous acid contains, therefore, the ions, H^+, ClO^-, HO^- and Cl^+. When we recall the nice balance which must exist between oxygen, with a kernel charge of six and only two electrons in its kernel, and chlorine with a kernel charge of seven and ten electrons in its kernel, we shall expect, also, the ions, HO^+ and Cl^-.

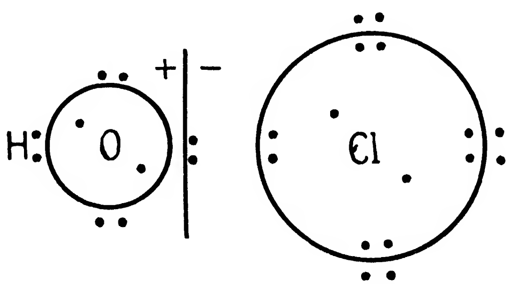


Fig. 16. Diagrammatic representation of the ionization of hypochlorous acid in oxidations.

By the union of this positive hydroxyl with the chlorine atom of another mol of hypochlorous acid, the compound $H:\overset{..}{\underset{..}{O}}:\overset{..}{\underset{..}{Cl}}\overset{+}{:}\overset{..}{\underset{..}{O}}:H$, would be formed. In this compound the

chlorine atom is positive because it has two covalences and only four unshared electrons. One of the hydrogen atoms would be easily lost to balance the chloride ion left by the molecule of hypochlorous acid which gave the positive hydroxyl. This would leave a semipolar union between the chlorine and oxygen. A repetition of this would give chloric acid. This has a high ionization constant because of the accumulation of semipolar oxygen atoms, and the chloric acid ion is

$$\begin{array}{c} \overset{-\,\cdot\cdot}{\underset{\cdot\cdot}{:O}}:\overset{\cdot\cdot +}{\underset{\cdot\cdot +}{Cl}}:\overset{\cdot\cdot\,-}{\underset{\cdot\cdot}{O}}:. \\ :\underset{\cdot\cdot\,-}{O}: \end{array}$$

3. Oxidation by Semipolar Oxygen Atoms. When potassium chlorate is kept at its melting point, in the absence of a catalyst, it may be largely converted to potassium perchlorate. This may be explained by supposing the transfer of an electrically neutral oxygen atom from one molecule of the potassium chlorate to another.

$$K^+.\ \begin{array}{c} \overset{-\cdot\,\cdot +\,\cdot\cdot\ \ \cdot\cdot\,-}{:O:Cl:O:} \\ \underset{\cdot\cdot +\,\cdot\cdot\ \ \cdot\cdot}{} \\ :\underset{\cdot\cdot\,-}{O}: \end{array} + \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}: = K^+.\ \begin{array}{c} \overset{\cdot\cdot\,-}{:O:} \\ \overset{-\cdot\,\cdot +\,\cdot\cdot\ +\cdot\,\cdot -}{:O:Cl:O:} \\ \underset{\cdot\cdot +\,\cdot\cdot\ \ \cdot\cdot}{} \\ :\underset{\cdot\cdot\,-}{O}: \end{array}$$

The oxidation of alcohols by nitric acid, potassium permanganate and other agents which contain semipolar oxygen atoms is probably of this type.

The presence of oxygen in a carbon compound enhances the tendency of the hydrogen atoms attached to the same or to adjacent carbon atoms to separate as positive hydrogen ions. It is well known, of course, that the hydrogen of a primary or secondary alcohol or of an aldehyde group is easily replaced by hydroxyl. In the simplest case, methyl alcohol separates into $\begin{array}{c} H:\overset{\cdot\cdot\,-}{\underset{\cdot\cdot}{C}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H \\ H \end{array}$ and H^+. An electrically neutral oxygen atom, $\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:$, would engage the free electrons of

the carbon atom and would immediately pick up a hydrogen ion to balance the negative character it acquires by sharing a pair of electrons. In the compound which results,

```
  ..
 :O:H
  .. ..
H:C:O:H,
  .. ..
  H
```

the balance of the affinity of the carbon for the hydroxyl and of the oxygen for the hydrogen, which causes these to separate as water, leaving a double union between the carbon and oxygen, is well known. That the carbon is doubly united with the oxygen in aldehydes and ketones has been shown by Sugden.

Theoretically, any semipolar oxygen atom may separate with its six valence electrons without disturbing the electronic balance of the atom from which it separates.

Chronology

1729—Conductors of electricity, Gray.

1735—Vitreous electricity, Dufay.

1747—Positive and negative electricity, Franklin in a letter to Peter Collison in England.

1786—Current electricity, Galvani. Soon after, Volta's batteries.

1790—Dualistic system, Lavoisier.

1807—Older electrochemical theory, Davy. *Phil. Trans.*, 1807, **1**.

1812—Older electrochemical theory, Berzelius. *Schweigger's Jour.*, 1812, **6**, 119.

1834—Faraday's law. *Phil. Trans.*, 1834, **55**, 77; *Pogg. Ann.*, 1834, **33**, 149, 433, 481.

1840—Trichloroacetic acid, Dumas. *Ann. Chem.*, 1840, **32**, 101.

1840—Satirical letter, Wöhler ("S. C. H. Windler"). *Ann. Chem.*, 1840, **33**, 308. *Ber.*, 1932, 65A, 90.

1852—Valence, Frankland. *Ann. Chem.*, 1853, **85**, 364.

1858—Chains of atoms, Couper, *Phil. Mag.*, 1858, (4) **16**, 104.

1858—Chains of atoms, Kekulé. *Ann. Chem.*, 1858, **104**, 133; *Ibid.*, 1858, **106**, 129.

1859—Transference of ions, Hittorf. *Pogg. Ann.*, 1859, **106**, 337, 513.

1878—Cathode rays, Crookes. *Chem. News*, 1879–80.

1887—Ionization, Arrhenius. *Ztschr. physik. Chem.*, 1887, **1**, 637.
1895—X-rays, Röntgen.
1895—Oxygen ions in the formation of ozone, van't Hoff. *Ztschr. physik. Chem.*, 1895, **16**, 411.
1897—Electrons, J. J. Thomson. Phil. Mag., 1897, (5) **44**, 293. Kaufmann. *Ann. Physik.*, 1897, **61**, 544.
1898—Radioactivity; radium Becquerel, Curies. *Compt. rend.*, 1898, **127**, 175.
1901—Positive chlorine in nitrogen trichloride, Noyes, Lyon. *Jour. Am. Chem. Soc.*, 1901, **23**, 463.
1901—Positive and negative halogen atoms, Stieglitz. *Jour. Am. Chem. Soc.*, 1901, **23**, 797.
1901—Positive and negative bromine, Lapworth. *Jour. Chem. Soc.*, 1901, **79**, 267.
1904—Electrons and chemical compounds, J. J. Thomson, *Phil. Mag.*, 1904, **7**, 237.
1904—Formation of ions during reactions, Noyes. *Chem. News*, 1904, **90**, 228.
1910—Electronic theory of combination, Falk, Nelson. *Jour. Am. Chem. Soc.*, 1910, **32**, 1637.
1911—Electronic theory of combination, Fry. *Ztschr. physik. Chem.*, 1911, **76**, 385; *Jour. Am. Chem. Soc.*, 1912, **34**, 664.
1913—Possibility of an electromer of nitrogen trichloride, Noyes. *Jour. Am. Chem. Soc.*, 1913, **35**, 767; 1921, **43**, 1774.
1914—Beckmann Rearrangement, Stieglitz. *Jour. Am. Chem. Soc.*, 1914, **36**, 275.
1914—Amine oxides, L. W. Jones. *Jour. Am. Chem. Soc.*, 1914, **36**, 1268.
1915—Configuration due to polar valence, Noyes, Potter. *Jour. Am. Chem. Soc.*, 1915, **37**, 189.
1902–16—Polar and non-polar compounds, G. N. Lewis. *Jour. Am. Chem. Soc.*, 1913, **35**, 1448. Octet, shared electrons. G. N. Lewis. *Jour. Am. Chem. Soc.*, 1916, **38**, 762. Kossel. *Ann. Physik.*, 1916, **49**, 229.
1919—Covalences: development of the theory, Langmuir. *Jour. Am. Chem. Soc.*, 1919, **41**, 868, 1543.
1920—Nitrogen trichloride, Noyes and Haw. *Jour. Am. Chem. Soc.*, 1920, **42**, 2167, 2173.

1922—Positive character of nitrogen in the nitro group, Stieglitz. *Jour. Am. Chem. Soc.*, 1922, **44**, 305; Organic chemistry (Noyes), 1926, p. 187.

1922—Amphoteric hypochlorous acid, Noyes and Wilson. *Jour. Am. Chem. Soc.*, 1922, **44**, 1630. Balard. *Ann. chim. phys.*, 1834 (2) **57**, 271.

1923—Potential polar valences, Noyes. *Jour. Am. Chem. Soc.*, 1923, **45**, 2559; *Ztschr. physik. Chem.*, 1927, **130**, 329.

1924—Ionization of compounds in which nitrogen has four co-valences, Hantsch and Kalb. *Ber.*, 1899, **32**, 3117. Stewart and Maeser. *Jour. Am. Chem. Soc.*, 1924, **46**, 2583. Noyes. *Jour. Am. Chem. Soc.*, 1925, **47**, 3026.

1917—Electrons with orbits including two nuclei, Noyes. *Jour. Am. Chem. Soc.*, 1917, **39**, 879.

1923—Pairs of electrons rotating about two nuclei, N. R. Campbell. Nature, 1923, **111**, 569. Sidgwick. *Trans. Faraday Soc.*, 1923, **19**, 469. C. A. Knorr. *Ztschr. anorg. Chem.*, 1923, **129**, 109.

1923—Mixed double bonds, Lowry. *Jour. Chem. Soc.*, 1923, **123**, 822. *Trans. Faraday Soc.*, 1923, **19**, 488.

1923—Valence and the structure of atoms and molecules, G. N. Lewis. *Am. Chem. Soc. Monograph*, 1923.

1924—Parachor, semipolar bonds, Sugden. *Jour. Chem. Soc.*, 1924, **125**, 1177; 1925, **127**, 1528; 1927, 1173. Lippel. *Ztschr. angew. Chem.*, 1929, **42**, 849, 873.

1925—Optically active sulfinates with semipolar bonds, Phillips. *Jour. Chem. Soc.*, 1925, **127**, 2552. Harrison, Kenyon, and Phillips. *Jour. Chem. Soc.*, 1926, **129**, 2079.

1926—Quadrivalent boron atoms, Stock. *Ber.*, 1926, **59**, 2226.

1926—Interpretation of the structure of benzene by inclusive orbits, Pauling. *Jour. Am. Chem. Soc.*, 1926, **48**, 1132.

1926—Inclusive orbits, Grimm and Summerfield. *Ztschr. Physik.*, 1926, **36**, 52.

1926—Evidence for inclusive orbits from the ionization potentials of argon and methane, Glockler. *Jour. Am. Chem. Soc.*, 1926, **48**, 2021.

1922—Magnetic silver atoms, Gerlach and Stern. *Ztschr. Physik.*, 1922, **9**, 349, 353.

1926—Magnetic potassium and sodium atoms, Kunz, Taylor, and Rodebush. *Science*, 1926, **63**, 550.
1926—Magnetic hydrogen atoms, Phipps and Taylor. *Science*, 1926, **63**, 48.
1927—Relation of magnetic atoms to nonmagnetic molecules, Noyes. *Proc. Nat. Acad. Sci.*, 1927, **13**, 377.
1927—The electronic theory of valency, N. V. Sidgwick. Oxford Press, 1927.
1928—Der Aufbau der chemischen Verbindungen, Robert Müller. Stuttgart: Enke, 1928.
1928—Reactions of compounds with odd electrons, Noyes. *Jour. Am. Chem. Soc.*, 1928, **50**, 2902.
1929—Electronic interpretation of oxidation and reduction, Noyes. *Jour. Am. Chem. Soc.*, 1929, **51**, 339.
1929—Chemische Bindung als elektrostatische Erscheinung, A. E. van Arkel and J. H. de Boer. A German translation by Li Klemm and Wilhelm Klemm, of articles which appeared in *Chemisch Weekblad*, 1929. Leipzig: S. Hirzel, 1931. (The book is written from the point of view of Kossel's theory, with practically no use of Lewis's principle of shared electrons.)
1931—The nature of the electron bond in terms of the quantum mechanics, Linus Pauling. *Jour. Am. Chem. Soc.*, 1931, **53**, 1367, 3225. (References are given to similar conclusions by Heitler and by London.)
1933—Types of Chemical Reactions, Noyes, *Jour. Am. Chem. Soc.*, 1933; *55*.

CHAPTER V

THE EFFECT OF VARIOUS RADIATIONS ON CHEMICAL SYSTEMS

THE study of the effect of radiation on chemical systems is frequently referred to as Radiochemistry. Among the types of rays which have been investigated may be mentioned alpha, beta and gamma rays from radioactive substances, x-rays, ordinary and ultraviolet light and sound waves.

The oldest branch of radiochemistry is undoubtedly Photochemistry. Early studies in this field were of a purely qualitative character. Many different chemical substances have been exposed for varying lengths of time to sunlight and the nature of the products determined. These studies have been of value in systematizing the effect of light on organic compounds of certain types, but they have told us very little of a theoretical nature.

Before we start a discussion of the effects of visible and ultraviolet light on complicated systems, we might examine the relationship of electromagnetic radiation to simple molecules. In the chapter on atomic structure, we found that single atoms may exist in various stationary states. An atom in state I may absorb radiation and be transformed into state II. This produces an energy-rich atom which may revert to its normal configuration with the emission of radiation. Properly speaking, a chemical reaction is not involved.

Let us now consider a molecule made up of two atoms. For purposes of discussion the system may be considered as analogous to a dumbbell. Such a system is capable of at least three types of movement: (1) Rotation end over end. This movement is one which seems to require a relatively

small amount of energy. (2) There may be a vibration of the two atoms with respect to each other along the line joining them. This type of movement generally requires a larger amount of energy than rotation. (3) Since atoms are complex and are made up of positive nuclei and electrons, there may also be a change in the relationship of these charged particles to each other. This type of change requires, in general, more energy than either rotation or vibration. Increase in the energy of rotation and vibration does not seem to produce chemical effects.

Reactions which take place due to thermal agitation are of very great interest, both from theoretical and practical standpoints. A detailed discussion of this subject is beyond the scope of the present chapter, but it may be pointed out that no completely satisfactory *general* theory has yet been arrived at. When two molecules approach each other, the kinetic energy (including translation, vibration and rotation) may be effective in producing reaction. There are factors, such as attraction and repulsion between various parts of the colliding molecules, which must be considered in any complete theory. Thus, when two molecules of hydrogen iodide (HI) approach each other, a molecule of iodine (I_2) and a molecule of hydrogen (H_2) may result, without, however, postulating that free iodine atoms (I) or hydrogen atoms (H) are formed as intermediates. The atoms may exchange partners, as it were, by a process involving less energy change than would dissociation into atoms. Such thermal reactions are not to be confused with those forming the topic of interest in this chapter, where molecules may be thought of as acquiring energy from some outside source not dependent on collision with neighboring molecules. The statement, that increase in energy of rotation or vibration does not seem to produce chemical effects, does not exclude the possibility that some thermal reactions may be brought about by such means. Indeed, a sufficient

increase in energy of vibration will lead to dissociation and hence reaction.

When a molecule absorbs radiant energy sufficient to produce a change in the electron system, several different effects may be observed. Dissociation of the molecule into atoms may result. If dissociation is not produced as a primary effect, i.e., if the energy is insufficient, an excited molecule is formed. This excited molecule may either revert to the normal state with the emission of radiation, or it may collide with another molecule and undergo a chemical reaction.

Let us consider the action of bromine on hydrogen. At ordinary temperatures, in the absence of light, these substances may be left together without any noticeable production of hydrobromic acid. If the mixture is heated to a temperature of several hundred degrees, reaction takes place. Since bromine is dissociated into atoms at high temperatures, it is possible that the reaction may really be between molecular hydrogen and monatomic bromine. A careful study of this system reveals that this is probably the case.

As we mentioned above, there is no appreciable change in this system at ordinary temperatures *in the dark*, but reaction will take place if the mixture is exposed to light. Is it possible that the effect in this case is also initiated by the presence of bromine atoms? Experiments indicate that this question should be answered in the affirmative.

All wave-lengths which are absorbed by molecules do not produce atoms. Many molecules absorb radiation in the far infra-red (long wave-lengths) with a consequent increase in energy of rotation. By the quantum hypothesis (see Chapter II, page 47), the rotation may not be augmented by any arbitrary amount. The exact increase is specific for a given type of molecule and depends on the weights of the atoms and the distance between them. In other words, the moment of inertia of the molecule is important. There is a

series of rotation energies which will be possible for a given molecule, so that several wave-lengths are absorbed in the far infra-red. These all lie near each other and are nearly uniformly distributed.

Objection might be raised to this highly pictorial method of describing absorption in the far infra-red, but there is very good evidence in favor of the assumptions involved. For example, there are two types of chlorine atoms, of mass 35 and 37 respectively. Each kind will combine with a hydrogen atom to form HCl. Since, as pointed out in the preceding paragraph, the amount of rotational energy which a molecule is capable of absorbing depends on the masses of the constituent atoms, HCl^{35} should behave differently in this respect from HCl^{37}. Actually there are two series of absorptions for HCl in the far infra-red; the agreement with theory is excellent.

There is another absorption by molecules in the infra-red, but at wave-lengths much shorter than the ones which have just been discussed. This absorption will cause an increase in vibration of the atoms in the molecule in addition to augmenting the energy of rotation. Let us suppose that there are several different states of vibration, which we may designate by A, B, C, etc. Since the quantum theory prohibits any intermediate state, the vibrational energy added must change the molecule from A to B and not to any arbitrary configuration. These transitions are usually large compared to those of rotation. However, both rotational and vibrational energy may vary simultaneously. For vibrational change from A to B, there would be a series of possible variations of rotation and also for vibrational change B to C there would be another group of possible shifts in rotation. The absorption would occur then as one group of lines close together for all of which the variation in vibrational energy would be the same, but each line corresponding to a different rotational change. Another group of lines would correspond to a second vibrational change,

each line belonging to a different alteration in rotation. This may be diagrammed schematically as shown below. The number of the rotation state may vary only by one or, in some cases, zero.

There is a further series of wave lengths absorbed, usually in the visible or in the ultra-violet. In this region the electron configuration of the molecule is changed as well as the energies of rotation and vibration. Since the energy necessary to change the electron configuration is almost always large compared to that necessary to increase the rotation

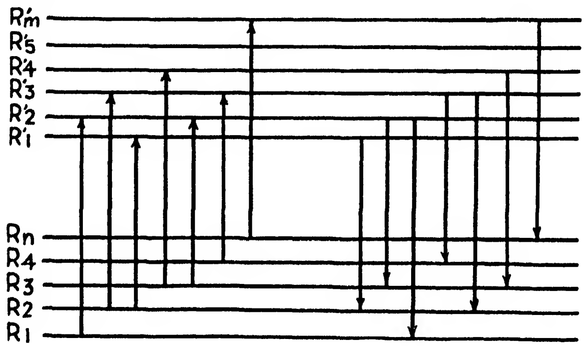


FIG. 17. Transition in a rotation-vibration band.

and vibration, we shall have a rather complicated system of absorption lines. Let us confine our attention for the moment to two different electron states which we will designate I and II in such a way that energy is *absorbed* in changing the molecule from I to II. Let A_1, B_1, C_1, etc. be the vibration states of the molecule in electron state I and A_2, B_2, C_2, etc. the vibration states of the molecule in electron state II. The character and spacing of the vibration levels in the two electron states will, in general, not be identical since by shifting electrons we change the force holding our atoms together. Finally let R_1^1, R_2^1, R_3^1 be the rotational levels for state I and R_1^2, R_2^2, R_3^2 be the levels for state II. More specifically the rotational levels will vary with the vibration level as well as the electron level, but we shall neglect this

fact for the moment. Now the transitions in an electron-vibration-rotation band would be from states in which the three kinds of motion are specified to another in which they are all different. Thus a state which we may designate as (I, A_1, R_1^1) may change to another designated as (II, A_2, R_2^2). As long as the electron and vibration transitions remain the same the lines will be close together and will constitute a *band*, for the changes in rotational energy are relatively small. Thus the lines of a band could be formed by the following set of transitions:

$$(I,\ A_1,\ R_1^1) \rightarrow (II,\ A_2,\ R_2^2)$$
$$(I,\ A_1,\ R_2^1) \rightarrow (II,\ A_2,\ R_1^2)$$
$$(I,\ A_1,\ R_2^1) \rightarrow (II,\ A_2,\ R_3^2)$$
$$(I,\ A_1,\ R_3^1) \rightarrow (II,\ A_2,\ R_2^2)$$
$$(I,\ A_1,\ R_3^1) \rightarrow (II,\ A_2,\ R_4^2) \text{ etc.}$$

If we substitute B_2 for A_2 we shall have a different band.

The fundamental idea back of this classification is similar to that underlying the Bohr theory of the atom. It is that the energy change of the molecule during a transition is equal to the energy of the quantum which is absorbed or emitted in the process. This is strictly analogous to equation (1) on page 50. Originally the methods used in quantizing molecular movements were similar to those used by Bohr for atoms (see equation (2), page 54). Just as the methods ran into difficulties for atoms, so there were disagreements between theory and experiment for molecules. The methods of new quantum mechanics must be used for the exact solution of molecular problems and the terms we have used such as rotation, vibration and electron state lose their original significance. It is possible, however, to extend the methods of the vector atom to molecules and arrive at a satisfactory correlation of *most* of their properties.

The complete, quantitative discussion of band spectra involves many details which we have not the space to consider. For example, molecules composed of atoms with nuclear spin show a peculiar behavior (see page 71). Sym-

metrical nuclear spin molecules do not change readily into the antisymmetrical form so that all rotation transitions are not possible. The symmetrical form will possess only odd numbers of units of rotation (1, 3, 5, etc.) while the antisymmetrical form will have only an even number of units (0, 2, 4, etc.). In this case the rotation state may change only by 0 or ± 2.

The bands we have discussed may occur either in absorption or in emission. That is, molecules will absorb certain wave-lengths when radiation consisting of all wave-lengths is passed through them. Under certain conditions they may be made to emit these same wave-lengths. In general emission spectra are more complex than absorption spectra because in a spark or arc the effective temperature may be quite high and the molecules be present in a number of different energy levels. In absorption, on the other hand, the molecules are initially only in those states in which they may exist at the temperature of the experiment, which is usually relatively low.

Continuous absorption is found in that region of wave-lengths which causes dissociation. Let us consider first a similar phenomenon exhibited by atomic or line spectra. Monatomic hydrogen will absorb several wave-lengths. The absorption line of longest wave-length will cause the transformation of atoms from energy level I to energy level II, the second line will cause changes from I to III, the third from I to IV, etc. Each successive energy level differs from the preceding level by a smaller amount than the one before, so that the absorption lines become closer and closer together as one proceeds to shorter wave-lengths (see Fig. 4, page 52). Finally the lines are so close together that they cannot be distinguished from each other and the series is said to *converge*. The limiting wave-length causes the transformation of the atom from state I to infinity, that is, the electron is removed from the atom. If, now, more energy is added (by the use of wave-lengths shorter than the

convergence limit) there is no definite quantized energy level to which the atom may be transformed since more than enough energy has been added to cause complete separation of the electron from the rest of the atom. The energy in excess of that necessary to cause such a separation must, therefore, appear as kinetic energy; that is, the shorter the wave-length of radiation below the convergence limit, the faster the electron and the rest of the atom will fly apart. Since it has not been found necessary to quantize energy of translation, any wave-length below that of the convergence limit may be absorbed and a region of continuous absorption is found.

In molecular spectra a somewhat similar description of the process of dissociation may be given. For any given electronic state of a molecule, there will be a series of vibrational energy levels, the spacing between them depending on the type of attraction existing between the two atoms making up the molecule. As more and more energy of vibration is added, the forces holding the atoms together become more and more inadequate to accomplish their duty, until finally the "elastic limit" will be exceeded and the atoms will separate. Thus in a band system, the first band may correspond to a transition from electron state I to electron state II and vibration state A_1 to vibration state A_2 (the lines in each band corresponding to rotation changes with which we are not now concerned). The second band in the system would involve the same electron change, but a vibration change from A_1 to B_2. The third band would produce vibration state C_2, etc. Since the vibration levels A_2, B_2, C_2, etc. grow closer together or converge in a manner depending on the characteristics of the molecule, the separation between successive bands becomes less as one proceeds to short wave-lengths, until finally a convergence limit will be reached just as in the case of the hydrogen atom. At the convergence limit the molecule will receive just energy enough to cause its separation into two atoms. Beyond this

limit (shorter wave-lengths) the atoms will fly apart with kinetic energy equal to the energy of the quantum absorbed minus the energy just sufficient to cause dissociation (equal to the quantum at the convergence limit).

Actual spectra may appear more complicated than that just described. For example, before a given band system reaches convergence, a new type of electron change may come into play, so that a new band system will start before the old one has proceeded to convergence.

The heat of dissociation of a molecule may be calculated from the wave-length of the convergence limit. When comparisons between thermal values and spectrum values of the energy of dissociation are available, the agreement is usually good.

We see, therefore, that absorption of light leads either to excited molecules or to dissociation. The excited molecules or the atoms may enter into reaction. One of the fundamental laws of photochemistry was first stated by Einstein. It says that the absorption of one quantum will cause one molecule to react. This statement should refer only to the process of activation or dissociation; in other words to the primary process. The chemical reactions which follow the first step may be of many types. To consider a simple case, oxygen molecules may be dissociated by the absorption of radiation of sufficiently short wave-length. We may write the equation: $O_2 + \text{quantum} = 2\ O$. This may be followed by the reaction: $2\ O + 2\ O_2 = 2\ O_3$. Thus for each quantum absorbed, three molecules of oxygen disappear and two of ozone are formed. Apparent variations from Einstein's law can, in many cases, be explained by simple mechanisms of this sort.

There are two classes of reaction which do not obey the simple form of Einstein's law even approximately. In one, the number of quanta absorbed greatly exceeds the number of molecules reacting. We may liken this type of reaction to the situation which exists when a weight is pushed up to

a mountain top. Once there, it may either slide back into the valley from which it came or it may slide over into a new one. For these reactions the molecules are activated by absorption of radiation, but only a few react, i.e., slide into the new valley, and the rest return to their original form, either with the emission of radiation or by losing the energy as kinetic energy. The efficiency of the process is smaller than one hundred per cent.

For the other class of reactions, the number of molecules activated by radiation is smaller than the number disappearing. A good example of this kind of reaction is that between hydrogen and chlorine, $H_2+Cl_2=2HCl$. Here the chlorine absorbs the light and enters into a process which starts off a long chain of spontaneous events. From 10,000 to 1,000,000 molecules react for each quantum absorbed, depending on conditions.

It is known that light affects a great number of chemical systems. The halogens, chlorine, bromine and iodine are all colored because they absorb visible radiation and they are quite light sensitive. Both activation and dissociation of these molecules are easily attainable with wave-lengths in the visible or near ultraviolet. Therefore nearly all reactions involving halogens may be accelerated by the use of light. This includes many different reactions with organic compounds, such as substitution or addition.

It would not be useful to give a complete list of gas reactions which occur under the influence of radiation. We may mention one phenomenon which is of great interest in photochemistry. If a tube containing a mixture of mercury vapor and hydrogen is exposed to radiation from a cooled mercury arc lamp, one line in the mercury spectrum is highly absorbed by the mercury vapor in the tube. In this way excited mercury atoms are produced. Upon collision between an excited mercury atom and a hydrogen molecule, the energy is transferred from the former to the latter, resulting in the production of hydrogen atoms. The presence

of an active form of hydrogen may be demonstrated by allowing it to react with certain metal oxides and other substances toward which ordinary hydrogen is inert. This process may be represented schematically as follows:

$$Hg + \text{quantum} = Hg\ (\text{excited})$$

Hg (excited) $+ H_2 = Hg + 2H$. $2H + CuO = Cu + H_2O$. This type of phenomenon was first predicted upon theoretical grounds by two German physicists, Klein and Rossland. It was later demonstrated experimentally by two other Germans, Cario and Franck. Since that time the phenomenon has been found to be quite universal. Oxygen and hydrogen may be made to combine at temperatures slightly above that of the room (45°C.); not only will hydrogen add to ethylene ($C_2H_4 + 2H = C_2H_6$) but the ethylene itself polymerizes to give higher hydrocarbons; excited mercury will induce a large variety of decompositions; ozone is produced by the action of excited mercury on oxygen. This is but a partial list of the many results in this field. It is fair to say, however, that a new field of photochemistry has been opened up by the pioneer work of Cario and Franck. The whole phenomenon is referred to as *photosensitization*. It is not confined to excited mercury, however. Chlorine will photosensitize the decomposition of ozone into oxygen; nitrogen dioxide will permit nitrogen pentoxide to be decomposed by visible light. The list of such sensitized reactions is steadily increasing.

One theoretical point in connection with photosensitization seems obvious. If the excited mercury is to dissociate the hydrogen, it must be capable of giving up sufficient energy to accomplish that task. This is the case from what we know of the energy required to split a hydrogen molecule into atoms and the magnitude of the quanta absorbed by the mercury.

The photochemistry of liquids and solids is of great interest, although the theoretical interpretation of the experi-

mental facts is somewhat more difficult than in gases. We have referred to the relationship between rotation, vibration and electron structure on the one hand and the absorption of radiation on the other. For solutions, no clear-cut theory of this type has been evolved. It is generally assumed that the effects are the same in liquids as for gases, but the various energy levels do not seem to be as clearly defined. Absorption spectra of liquids usually do not consist of distinct lines, but of broad bands covering a range of wave-lengths. In general, it is difficult to tell where absorption begins and where it ends, for the amount seems gradually to diminish as the wave-length is changed and to approach zero very slowly. Liquids and dissolved substances do, however, have characteristic absorption spectra.

Studies of the absorption spectra of organic liquids have revealed that similarities exist between all of the acids; that the aldehydes fall in a class, etc. When a given molecule is both an aldehyde and an acid, it shows a somewhat modified absorption, characteristic of both classes of compounds. A great deal of interesting information is obtainable from absorption spectra.

The photochemical effects in solution and in pure liquids are of interest, particularly since many natural phenomena occur in the liquid phase. Here again similar types of compounds undergo the same general reaction. Organic acids (with the exception of formic, which decomposes in two ways) always seem to lose carbon dioxide under the influence of ultraviolet radiation. The efficiencies (number of molecules decomposed per quantum absorbed) are by no means identical. Simple organic acids such as acetic (CH_3CO_2H), propionic ($CH_3CH_2CO_2H$) and butyric ($CH_3CH_2CH_2CO_2H$) decompose very slowly, whereas the acids with two carboxyl groups such as oxalic (HO_2CCO_2H) and malonic ($HO_2CCH_2CO_2H$) react much more readily.

Other types of organic compound decompose in characteristic fashion. Aldehydes undergo two types of reaction,

one of polymerization (formation of more complex molecules without change in empirical formula) or decomposition by losing carbon monoxide. The list could be extended to other types.

Many inorganic photochemical reactions in solution, or of solids, are also known. The commonest is the reaction in the photographic plate in which the silver salts of chlorine and bromine give metallic silver with evolution of chlorine or bromine. The commercial importance of this reaction needs no emphasis. Investigations of the mechanism are numerous, for the image does not appear until the plate is developed. The initial effect of the light must be small, perhaps forming nuclei of silver in certain crystals.

The phenomenon of photosensitization also occurs in solution. The decomposition of oxalic acid is considerably accelerated by adding small amounts of uranyl sulfate (UO_2SO_4). Whether uranyl sulfate absorbs the radiation and transfers its energy to oxalic acid molecules upon collision is not entirely clear. It seems more probable that a light sensitive complex molecule exists in solution. Very little is known at present with regard to the nature of excited molecules in solution and the speeds with which they move about. The application of mathematics to photochemical processes in such cases rests, therefore, upon a somewhat unsatisfactory basis.

No discussion of photochemistry would be complete without some reference to the subjects of photosynthesis and the use of radiation in medicine. It is a well known fact that carbon dioxide reacts with water in plants to give carbohydrates and oxygen and that sunlight is a necessary factor. Much work has been done in the laboratory in an endeavor to reproduce this reaction *in vitro*.

It was assumed at first, by von Bayer, that carbon dioxide reacts with water under the influence of radiation to give formaldehyde and oxygen. $CO_2 + H_2O + \text{light} = HCHO + O_2$. The next step was supposed to be a polymerization of

the formaldehyde to carbohydrates. The latter reaction can be reproduced in the laboratory, although the amount of carbohydrate formed is very small and a large number of different substances always results. It is possible to cause the formation of carbohydrates from formaldehyde by other chemical means, although conditions for the reaction differ widely from those existing in plants.

Regarding the first reaction, that is the formation of formaldehyde, some doubt seems to exist. A few years ago English workers reported that upon passing carbon dioxide into water, in the presence of radiation from a quartz mercury arc lamp, small amounts of formaldehyde were formed. This statement has been called into question, particularly by workers in California. It seems that formaldehyde is not formed directly, especially if the carbon dioxide and water are carefully purified.

Other work indicated that the reaction between carbon dioxide and water could be made to take place under the influence of light if certain colored salts (usually carbonates) were present. Such experiments would be of importance because plants contain a green compound, chlorophyll, which is supposed to play an important part in the photosynthesis of carbohydrates. It is uncertain at the present time just what interpretation may be given to this work. During the past few years, however, organic chemists have succeeded in dissecting chlorophyll molecules in such a way that a great deal is now known concerning their structure. The exact mechanism of their action in making photosynthesis possible is still uncertain, although several very interesting ideas have been advanced. Perhaps the most plausible tells that there is a reaction which does not involve light in which the chlorophyll reacts with carbon dioxide in the presence of an enzyme (catalyst) to give water, carbohydrates and a dehydrogenated chlorophyll. The dehydrogenated chlorophyll then reacts with water in the presence of light to give back chlorophyll with the liberation of oxygen. This theory

accounts satisfactorily for most of the known facts concerning photosynthesis.

Ultraviolet radiation is now widely used by medical men. In one case, at least, it is known to be of positive benefit, namely in the cure and prevention of rickets. In this disease, the bones do not develop normally and stunted growth and malformation result. It is especially prevalent in large cities where the children are not exposed to sufficient sunlight and, in industrial communities, where the proper food is not consumed. It has been known for a long time that certain foods possessed antirachitic properties. One of these is cod-liver oil. It is also known that only certain wavelengths in the sun's rays are effective in preventing rickets and that these are the very short ones which do not traverse window glass.

A certain substance, vitamin D, is supposed to be effective in preventing and curing rickets. Researches on its isolation are numerous. They all agree that it is a substance which occurs in some fats, but that it is probably an alcohol. A large class of compounds, the sterols, is known to have many of the properties associated with vitamin D. Of these, cholesterol was thought for a time to be the substance in question. Careful investigation of the cholesterol used has shown, however, that another substance, ergosterol, was present in small quantities. Isolation of the latter is a difficult matter, but it has been purified to such an extent that 1/50000 of a milligram per day (after exposure to ultraviolet radiation) will cure rickets in a rat in the course of a few weeks. Investigations by Professor Windaus and his students at the University of Göttingen in Germany seem to indicate that irradiated ergosterol is really vitamin D. The exact chemical structure of this compound is not known, although many of its properties have been studied. Both the formation and decomposition of vitamin D are brought about by ultra-violet radiation so that its concentration never reaches a high value.

It is known, however, that certain foods such as oats, yeast and cod-liver oil are effective in preventing rickets after they have been exposed to ultraviolet radiation. Exposure of children to ultraviolet radiation for a short time each day will also prevent rickets.

Various statements in the literature have been shown to be inexact. It was thought by one observer that merely shining ultraviolet light on a cage with the rat removed was sufficient to cure any rat which used the cage subsequently. It seems, however, that the cage must be dirty in order to accomplish this end and the fat left on the walls did acquire antirachitic properties. The rat was cured by the substances he absorbed in licking the walls.

The use of radiation, both infra-red and ultraviolet, has been prescribed frequently to aid in building up general health and to help overcome deep-seated infections. The usefulness of this treatment has never been thoroughly demonstrated, for very few controlled experiments have been carried out. The ordinary criterion of the effectiveness of the treatment is erythema or sun-burn, but one who has studied photochemistry will recognize that wave-lengths which produce one reaction do not necessarily produce all reactions. Hence the beneficial effects of the treatment, if any, may be entirely independent of the extent to which the skin is tanned. More work is necessary in this field, for accurate, quantitative data on the physiological effect of radiation, other than in rickets prevention, are not available. At present, it is impossible to dissociate psychological effects from those which are really physiological. The use of ultraviolet in treating certain skin afflictions, such as ringworm and eczema, is undoubtedly of much benefit. It is also known that ultraviolet light has some definite bactericidal properties.

Some attention has been given to the chemical effects of other types of radiation than visible and ultraviolet light.

X-rays are rather violent in their action on matter, for the energy associated with them is large.

X-rays have proved to be a useful tool in solving many different problems. When a beam of x-rays is passed through a crystal, scattering occurs. The kind of scattering is dependent on the wave-length of the x-rays, the distance between the atoms and the type of crystal. It is thus possible to determine the nature of the crystal lattice by their use. Such studies are of great practical as well as theoretical interest. The strength of a piece of metal is dependent, among other things, upon its crystal structure. X-rays may be used, therefore, to indicate possible points of weakness. Further applications have been made in the textile industry and in ceramics.

The chemical effects of x-rays have not been thoroughly investigated. Most of the work consists in the observation of isolated interesting facts. It is known that many reactions may be initiated by the presence of ions and since x-rays produce ions in all matter through which they pass, they will cause chemical effects. Fundamentally, however, x-rays are so violent that many different simultaneous processes are apt to occur in a given system.

In biology it has been shown that x-rays will cause variations in certain species and that the mutations will breed true and not revert to the type of the ancestors. This has been demonstrated for a certain type of fruit fly by Muller of the University of Texas and for tobacco plants by Olson and Goodspeed of the University of California.

The chemical effects of the various rays from radioactive substances are of great interest. Of these, alpha particles have been more studied than the others. Alpha rays consist of helium atoms with two positive charges and they leave the radioactive substance from which they are emitted with very high velocities. In passing through gases (or liquids) they knock electrons out of the molecules they encounter.

These electrons may be picked up by other molecules, so that the result is the production of both positive and negative ions. If the ions are active chemically, one should expect to find some relationship between the extent of ionization and the number of molecules reacting. This law would be analogous to Einstein's law for photochemistry.

The amount of ionization produced by alpha particles in passing through gases has been quite thoroughly studied. It is possible to calculate the number of positive and negative ions formed with fairly high accuracy and to compare this with the number of molecules reacting. We shall consider only one example, the reaction between hydrogen and oxygen to form water. The passage of alpha particles through a mixture of hydrogen and oxygen will produce positive ions directly and, since oxygen has a tendency to pick up electrons, negative ions will also be formed. It is assumed that the next step is the formation of clusters on these ions. In other words the charged ions attract the neutral molecules in the neighborhood and form aggregates. These may be $(H_2 \cdot O_2 \cdot H_2)^+$ and $(H_2 \cdot \overset{-}{O_2} \cdot H_2)$, the charge being associated perhaps with the cluster as a whole for the positive group and localized on the oxygen molecule in the second. Reaction occurs when a positive and a negative cluster come together thus: $(H_2 \cdot O_2 \cdot H_2)^+ + (H_2 \cdot O_2^- H_2) = 4H_2O$. According to this theory, four molecules of water would be found for each pair of ions. The experimentally determined value is 3.85, which is in satisfactory agreement with the theory.

There are however, other explanations for this reaction and some definite objections may be raised to a mechanism involving ionic clusters.

Many other reactions have been investigated in a similar manner.

The chemical effects of beta rays have not been as thoroughly investigated. These rays are electrons. It has been shown that electrons will cause chemical reaction only if they possess sufficient kinetic energy. In photochemistry

we found that reactions are not produced unless the quanta absorbed were sufficiently rich in energy. In an exactly similar way, the electrons must move rapidly enough through the reacting system so that they can produce activation. Several reactions have been studied in this fashion.

Dr. W. D. Coolidge of the General Electric Company has recently developed a tube which makes it possible to obtain large numbers of rapidly moving electrons and to study their chemical effects. The tube is constructed very much like an x-ray bulb, but is fitted with a thin metal diaphragm at one end. High speed electrons will pass through this metal sheet in quite large numbers. Studies made with this apparatus are still somewhat qualitative in character, but results obtained indicate that a definite relationship between the number of ions produced and the amount of chemical action will be found in this case, as for alpha particles.

The chemical effects of gamma rays are little known, but should be analogous to those of x-rays. Interesting philosophical speculation as to the possible effects of the cosmic rays of Kolhörster and Millikan might be made. They may be analogous to x-rays but of very short wave-length and high penetration. (See page 86). Might it not be possible that changes in species of plants and animals and certain abnormalities might be brought about by the accidental action of cosmic rays on cells?

One other type of radiation remains to be considered: *sound*. Studies in this field are comparatively recent. Ordinary sound waves produce very few chemical effects. They may, if sufficiently intense, detonate explosives. As the frequency of the sound is increased far beyond the range of audibility it is found that many interesting phenomena are produced. Such sound waves will detonate explosive mixtures, cause many chemical reactions to take place and make liquids boil at temperatures much below the normal boiling point. The theory underlying these facts has never

been thoroughly investigated, but it seems that high frequency sound waves will affect a system in much the same manner as an increase in temperature. Researches on these phenomena indicate that the violent movement given to the molecules by the passage of high frequency compressional (sound) waves will lead to many unexpected chemical effects. For example the rate of hydrolysis of dimethyl sulfate ($(CH_3)_2SO_4$) seems to be accelerated.

We have done little more than indicate that light waves, alpha, beta and gamma radiations, x-rays and sound waves may induce very interesting chemical effects. Both from the standpoint of theory and the standpoint of practice this entire field is undergoing a very rapid development. The practical applications may be among the most interesting future achievements. Happily the world is not faced with a fuel shortage, but in the dim and distant future the careful utilization of the sun's energy may be of prime importance to mankind. In medicine only a beginning has been made and much careful work is needed to distinguish truly beneficial effects from fads. One might continue a recitation of the possibilities which the study of the effects of radiations holds for humanity, but we shall content ourselves with the mere statement that the list of such possibilities would be a long one.

References

Kistiakowsky, G. B. *Photochemical processes.* New York: Chemical Catalog Co., 1928.

Spoehr, H. A. *Photosynthesis.* New York: Chemical Catalog Co., 1926.

Lind, S. C. *The chemical effects of alpha particles and electrons.* New York: Chemical Catalog Co., 1928.

Richards, W. T., and A. L. Loomis. "The chemical effect of high frequency sound waves." *Jour. Am. Chem. Soc.*, 1927, **49**, 3086.

Baly, E. C. C. "Photosynthesis." *Chem. News*, 1928, **137**, 27, 43.

Style, D. W. G. *Photochemistry.* New York: Dutton, 1931.

Chapter VI

NEW ELEMENTS AND NEW USES FOR OLD ONES

The *Ancients* knew only seven metals which we now regard as elements: copper, gold, silver, iron, lead, tin and mercury. They knew, also, two other elements, sulfur and carbon, but they did not know that diamonds, graphite and charcoal are different forms of the same element and did not recognize any of these elements as the unchanging and unchangeable entities which they still remain in spite of the transmutations of elements discovered during the twentieth century.

The *Alchemists* added only one element, arsenic, to this list. Basil Valentine, one of the *iatrochemists*, recognized three others, antimony, bismuth and zinc. Platinum was discovered in the sixteenth century. Thus we see that only 14 were known before the eighteenth century.

It has been shown, in previous chapters, that the number of elements in the universe is probably limited to 92. The discovery of all of these has been announced but there are several which have not yet been isolated, even in the form of pure compounds.

During the seventeenth and eighteenth centuries, the idea of chemical elements slowly emerged and the number distinguished was gradually enlarged. Richter gave the combining weights of eight acids and eight bases but the free elements corresponding to these, with two or three exceptions, were not isolated until later. Fluorine, indeed, was not isolated until 1886, although it was recognized as an element and its atomic weight had been determined before that.

During a short period in the eighteenth century, known

as that of *pneumatic chemistry*, hydrogen, nitrogen, oxygen and chlorine, the common and most important elements which are gaseous at ordinary temperatures, were identified.

During the eighteenth and nineteenth centuries, about 45 elements were discovered by *analytical* methods, frequently by the careful examination of characteristic minerals.

The development of the *spectroscope* by Bunsen and Kirchoff, about 1860, soon led to the discovery of six elements, rubidium, cesium, thallium, indium, gallium and helium. The last was discovered by Lockyer in the sun nearly 30 years before Ramsay found that it is a constituent of cleveite and uraninite.

The *Periodic System* of Newlands, Mendeléeff and Lothar Meyer, became of great service in predicting the properties of new elements, and after Rayleigh and Ramsay had been led to the discovery of argon by Rayleigh's careful determination of the density of nitrogen, the system became in Ramsay's hands a reliable and indispensable guide in the discovery of the other five *noble gases*.

The discovery of the phenomena of *radioactivity* by Becquerel, quickly followed by the isolation of radium by the Curies and the hypothesis of radioactive disintegration proposed by Rutherford, has been the starting point for the characterization of 12 elements forming 40 or more individuals, by means of their radioactive properties. These twelve elements have atomic numbers ranging from 81 to 92 and atomic weights between 206 and 238. The individuals include many isotopes, and while isotopes are indistinguishable in their chemical properties, they may differ in their rates of radioactive disintegration.

The periodic table, in spite of its great usefulness in predicting unknown elements between the atomic numbers 1 and 54, was less certain beyond that point. In this region, the *atomic numbers* have fixed definitely the number of ele-

ments which there is any hope of finding below uranium. The *x-ray spectra* of the *K* series are supposed to be due to two electrons close to the nucleus of each atom. Moseley showed that there is a nearly linear relation between the square roots of the frequencies of the vibrations causing the x-ray lines due to these electrons and the atomic numbers of the elements. This has fixed a definite limit to the number of elements which are still unknown. These facts have been of service recently in the discovery of hafnium, masurium, rhenium and illinium necessary to fill out the Periodic Table. Announcements have been made of the discovery of Nos. 85 and 87 by a magneto-optic method and of the discovery of No. 87 by more common methods. Mendeléeff was uncertain about the number of elements between barium and tantalum. Only four elements were known in this region when the periodic table was first published, but Mendeléeff thought 20 elements were possible. The atomic numbers, based on the x-ray spectra, made it evident that there can be only 16 and of these 14 were already known. Quite recently, the other two have been found.

Hafnium. Before the number of elements possible in this region had been established by means of the x-ray spectra, Urbain and Auer von Welsbach separated the element, called at that time ytterbium, into two parts, named by Urbain neoytterbium and lutecium and by von Welsbach, aldebaranium and caseopeium. The names ytterbium and lutecium were adopted by the International Committee.

In 1911 Urbain believed that he had found a third element in the same material and proposed to call it celtium. This was supposed to belong to the rare earth group. In 1922 Bohr's theory of the electronic structure of atoms led him and Hevesy to the conclusion that element No. 72 should not be found among the rare earth group but that it should resemble zirconium. This suggested the examination of zircon for the missing element. Hevesy and Coster found x-ray lines characteristic of element 72 in the first sample of

Norwegian zircon that they examined and they were able to show that many other zircons from widely different localities, and also purified zirconium compounds, contain the new element, to which they gave the name *hafnium.*

It will be seen from the above that both Bohr's theory of the electronic structure of atoms and Moseley's relation between x-ray spectra and atomic numbers contributed to the discovery of hafnium. It was the first and probably will remain the only element discovered on the basis of its electronic structure. X-ray spectra have aided in the discovery of three other elements.

For the separation of hafnium from zirconium, it was necessary to discover a compound which could be crystallized repeatedly without decomposition. Ordinary salts of these elements are so easily hydrolyzed that they are not suitable for this purpose. The salts in which zirconium and hafnium form part of the anion are more stable and the first successful separations were made by using ammonium and potassium hexafluozirconates and hexafluohafnates, $(NH_4)_2HfH_6$ and K_2HfF_6. These are analogous to the fluosilicates and illustrate the close relations between silicon, zirconium and hafnium.

Masurium and Rhenium. Manganese occurs in the subgroup of the seventh column of the Periodic Table. Its atomic number is 25 and its atomic weight 54.93. It is, of course, a metal and, while not exceedingly abundant, its existence has been known to chemists since its characterization by Scheele in 1774. In fact, the element seems to have been familiar to the ancients, and its compounds were used by them in glass making. Below manganese in the table there is room for two elements, No. 43 and No. 75. The discovery of these elements was long awaited by chemists.

In 1925 announcement of the discovery of elements 43 and 75 was made by Noddack and by Noddack and Berg, in Germany. They were named Masurium, Ma, and Rhenium, Re, respectively. Their identification was made

by several physical and chemical properties. A beginning of a systematic study of its compounds has been made.

By a study of the geochemistry of the elements, it was concluded that these two missing elements might be found associated with the elements of the platinum group, such as ruthenium and osmium. A systematic investigation of several minerals, such as gadolinite and columbite, showed beyond doubt that the elements 43 and 75 were present. As in the case of the discovery of hafnium and illinium, x-ray spectroscopy gave the decisive proof of their existence. Rhenium has now been obtained in sufficient quantities for the quotation of some of its compounds for sale.

The atomic weight of rhenium is now given in the International Tables as 188.7, based on a determination by Noddack and Noddack. There is still some question as to the purity of the preparations of these two elements, so that this figure may be subject to revision in the future.

Illinium. The Rare Earth Group presents a baffling challenge to the chemist because it contains a large number of elements whose properties are almost identical. We know many smaller groups in which there is such a close relationship that the separation of chemical individuals requires the utmost skill and patience, but the Rare Earth Group is unique in the fact that it is composed of a large number of individuals whose properties show such gradual changes that the ordinary methods of separation are useless. The preparation of any member of the group in a high state of purity is a task which presents many difficulties and requires long and painstaking effort. Most of the members of the group have been separated successfully from their near neighbors, but it is quite certain that several of the less abundant ones have never been completely isolated, in spite of years of the most exacting effort in many laboratories. The methods of separation depend upon slight differences in solubility of the salts or upon slight changes in the basicity of the elements themselves. Fractionation methods

are necessary and, as a consequence, the separations are slow and incomplete, while there is always involved a large and disheartening loss of material through the intermediate fractions. Countless repetitions—literally tens of thousands of crystallizations—a combination of methods and a skillful utilization of the properties of some of the more abundant elements are necessary in order to approach a state in which the separations are complete.

Early students of the Rare Earth Group noticed that the elements neodymium and samarium showed greater differences than can be found in any other pair of adjacent elements. If the group is arranged in the order of the solubility of any of its salts or in the order of the precipitation by ammonia, or the hydrolysis of the nitrites, or the thermal decomposition of the nitrates, there is always a noticeable break between neodymium and samarium. So striking was this phenomenon that it led to the prediction of the existence of an unknown element between these two elements. Efforts to locate such an element were unsuccessful, but as the problem was investigated it seemed possible that this space might be large enough for two elements.

After Moseley had shown that the atomic number of an element may be determined by the frequency of the vibrations causing the lines of its x-ray spectrum, it became almost certain that the space between neodymium, No. 60, and samarium, No. 62, was occupied by a single unknown element. Interest in the identification of this element was greatly increased by Moseley's work and renewed efforts were made to find this elusive member of the rare earth family.

Work upon the rare earths was begun at the University of Illinois in 1909, under the leadership of Professor Clarence W. Balke. As a result of long and faithful effort, there was accumulated a considerable quantity of material which included relatively pure compounds of several members of the group. Several of the purest of these were sent to the

United States Bureau of Standards, following a cooperative plan which had as its object the mapping of the red and infra-red regions of the spectra of the elements. The results were published in the Scientific Papers of the Bureau. Particular interest centers about the work on the salts of neodymium and samarium. For each of these, there were reported about 1500 lines whose origin is attributed to these elements. In addition to these, there were 130 faint lines of unknown origin, which were common to the spectra of both elements. These could not be identified as belonging to any known element, but their presence seemed to justify the conclusion that the supposedly pure salts of neodymium and samarium contained a common impurity. Concerning these lines, Dr. C. C. Kiess wrote, "While it would be a hasty conclusion to regard these lines as characteristic of a new element, yet this idea seems plausible in view of the fact that the present accepted scheme of the periodic table of elements requires a new element of atomic number 61 between neodymium and samarium."

Following this suggestion, work was begun on the concentration and identification of the substance which produced these unknown lines. Dr. L. F. Yntema, working as a Fellow of the National Research Council, carried out an x-ray examination in the Sloane Laboratory of Physics at Yale, while fractionations were continued at the University of Illinois. The result of two years' work was the addition of five arc spectrum lines toward the violet and the conclusion that if No. 61 were present at all it must be in quantities of less than one part in a thousand.

It was evident that some method of obtaining a greater concentration must be found before the identity of the element could be established. The usual method of fractionation is by means of the double magnesium nitrates, whose solubilities should bring the element No. 61 between neodymium and samarium. Both of these elements are relatively abundant and have prominent and persistent ab-

sorption spectra. It seemed probable that the spectrum of a very rare element falling between these two might easily be concealed by those of its more prominent neighbors. Consequently, Dr. J. Allen Harris, working with Professor B. S. Hopkins, carried out an extensive fractionation of the bromates, by means of which neodymium is effectively separated. While the work was progressing, there was obtained a new absorption line at 5816 Ångstrom units. This grew stronger as the work was continued and another line at 5123 Ångstrom units was observed later. The x-ray examination of the material produced in this way gave lines which were in close agreement with the calculated values for $L\alpha_1$ and $L\beta_2$ of element No. 61. Careful study of these lines was necessary to make certain that they were not produced by other elements, whose first, second or third order lines might easily be mistaken for those of element No. 61. After eliminating these possibilities, it was concluded that the most elusive and least abundant element of the Rare Earth Group had finally been identified. The name *Illinium* was given to the new element.

Within a few months after the announcement of the discovery, similar conclusions were reached in three other laboratories as the result of work which was done simultaneously and independently. Professor Charles James and H. C. Fogg at the University of New Hampshire, in the course of their extended and brilliant work upon this group, saw indications of the presence of illinium in their materials, which had been extracted from gadolinite, xenotime and monazite. Samples were submitted to Professor J. M. Cork of the University of Michigan. He examined them in his well equipped x-ray laboratory and obtained distinct lines of the *K* series for element No. 61. This is convincing proof of its presence since the lines of this series are much more characteristic than the lines of the *L* series.

In the Berlin laboratory of R. J. Meyer, similar work had been in progress with material from the same minerals and

with the use of the same methods of fractionation. They also obtained clear x-ray spectral lines in the *K* series for element No. 61.

Professor Rolla at the University of Florence worked on some neodymium-samarium materials which he had obtained from monazite. These he fractioned as the double thallium sulfate. From his fractions, x-ray evidence for the existence of element No. 61 was obtained, but he was, evidently, not very certain of his first results, because they were not published but were sent in a sealed communication to the Italian Academy of Science. He began work at once on a larger quantity of material and later confirmed his early conclusions. After the announcement of the findings of Harris, Yntema and Hopkins, the sealed communication was published and priority was claimed. The name *Florentium* was suggested for the new element.

Professor Rolla states that he began his work in 1922 deposited his sealed communication in 1924, and the publication is dated November, 1926. The publication of the wave-lengths of the 130 spectral lines by the Bureau of Standards was dated January 6, 1922, and those of the five additional lines, September 29, 1923, while the complete scientific evidence was published in June, 1926.

Element 87. The discovery of this element, which belongs to the potassium group and completes that group of elements, has been recently announced at Cornell University by Jacob Papish and Eugene Wainer. The following statement is taken from their preliminary paper.

"Ten kilograms of finely ground samarskite was heated in a stream of dry hydrochloric acid at a temperature of about 1000°. The volatile products were converted into sulfates and upon spectroscopic examination were found to contain potassium and rubidium; the lines of cesium were doubtful because of spectral interferences. The soluble sulfates were extracted with water, and to the solution ammonium hydroxide was added to slight excess. The precipitate, mainly

hydrated ferric oxide, was removed by filtration, ignited and washed with hot water. The washings were added to the ammoniacal filtrate."

From this solution a portion containing element No. 87 was separated from a part of the other elements present by fractional crystallization of the sulfates, perchlorates and alums. The material was then subjected to x-ray spectrographic tests and gave conclusive evidence of the presence of the element sought. A name has not yet been assigned to the element.

Fred Allison and E. J. Murphy, sometime earlier, announced the discovery of No. 87 in pollucite and lepidolite and of No. 85 in potassium bromide. They have suggested the name *Virginium* for the former and *Alabamine* for the latter. They detected the elements by a magneto-optic method.

New Uses for Tantalum and Columbium. Sometime in the eighteenth century, a black mineral found its way from Massachusetts to the British Museum. In 1801 Hatchett examined this mineral and prepared from it an impure oxide of a metal, which he named columbium because the mineral came from America. The following year, Ekeberg, in Norway, obtained from a similar mineral an impure oxide of another metal, which he called tantalum because of the tantalizing difficulties met in separating it from its associates. In 1844 H. Rose distinguished two elements in a sample of columbite which he examined. One of these was the tantalum of Ekeberg and the other was the same as the columbium of Hackett. Rose called it, however, niobium, a name still used in Germany.

In 1903 von Bolton, in Germany, developed a method for preparing ductile tantalum and on account of its ductility, high melting point and slight volatility, it soon came into use for the filaments of electric light bulbs. It was the first successful substitute for the carbon filament invented by Edison. Millions of these tantalum bulbs were made in

Germany and America. It was not long, however, before tantalum was completely displaced by tungsten, which has a melting point of 3370°C., the highest melting point of any metal known. The boiling point of tungsten is 5900°, 1500 to 2000° higher than that of carbon and its unique value for the filament of electric light bulbs is apparent.

About 1904 Clarence W. Balke undertook a study of compounds of columbium and tantalum and methods of separating them, under the direction of Edgar F. Smith. With the material prepared, Dr. Balke determined the atomic weight of columbium as 93.5, a value which was at once accepted by the International Committee on Atomic weights. That value was changed to 93.1 on the basis of a determination of Edgar F. Smith and W. K. van Haagen by a method believed to be more accurate.

In 1920 Professor Balke and his associates in the laboratory of the Fansteel Products Company began an intensive study of the methods for the production of pure tantalum and of the properties and uses of the metal. This was done at a time of industrial depression and the Company deserves great credit for supporting Professor Balke in a very expensive, tedious research, the commercial results from which were very uncertain. Only a few of these results will be mentioned.

When two electrodes, one of lead and one of tantalum, are dipped into dilute sulfuric acid and connected with an electric light circuit furnishing an alternating current, the electricity will pass in only one direction. This gives a very efficient "rectifier" and the direct current which results may be used for charging the battery of an automobile, for radio sets, for railway signals and for many other purposes.

Tantalum at ordinary temperatures is more resistant to aqua regia than gold or platinum and is also resistant to nitric, hydrochloric or dilute sulfuric acid at their boiling points. This makes crucibles and dishes of tantalum very useful in the laboratory. These crucibles cannot, however,

be used for ignitions or fusions, as tantalum begins to oxidize in the air at 400°C.

The acid resistant and non-corrosive character of tantalum, combined with its hardness, have made tantalum spinnerets almost indispensable in the rayon industry.

Professor Balke has recently obtained columbium in a very pure form and in sufficient quantities to justify a consideration of its commercial possibilities. Both tantalum and columbium are probably more rare than gold.

The story of columbium and tantalum is an admirable illustration of what some one has called "scientific heredity." Professor Balke was the scientific son of Edgar F. Smith. Professor Smith was the scientific son of Wöhler.

High-Speed Steels. It has long been known that the properties of iron are so greatly modified by its combination with carbon as to make from it three different metals, wrought iron, steel and cast iron. When steel, containing about one per cent of carbon, is heated to a high temperature, the carbon combines with the iron and the compound formed dissolves in the iron forming a solid solution. If the steel in this condition is quenched in water, to carry it quickly past a temperature at which the carbon would segregate as iron carbide, the metal is very hard. Such steel is unstable, however, and at a temperature approaching redness the solid solution will separate into a mixture of pure iron and iron carbide, which is comparatively soft. The steel is said to lose its temper, and if this happens to a cutting tool used in a lathe which is run rapidly, the tool becomes useless.

It has been found that the addition of tungsten, chromium, molybdenum and of some other elements in proper proportions prevents this segregation of the carbon. Tools made on the basis of this principle will retain their hardness even when the lathe is run at a rate which causes the tools to become almost red hot. Such steels are called "high speed steels." The saving of the time of expensive ma-

chinery and of high-priced workmen which the use of these tools has made possible has been worth vast sums of money to manufacturers. The statement has recently been made of high speed steel that, "It has played a major rôle in our economic civilization, and it has done, perhaps, more than any one other development in the last twenty-five years, to help make men independent and to help make the expenditure of a given amount of human energy produce more of the necessities and luxuries of life."

Recently, a method of making tungsten carbide, which is very hard, and of sintering it with about 15 per cent of cobalt, has been discovered. This material is called "bonded tungsten carbide" and is very much harder than any kind of tool steel. The hardness is retained even at a red heat. It may replace the high speed steels for many purposes and has a number of uses for which it is very superior.

Bonded tungsten carbide has been used for making dies for drawing fine wire. Such a die, after it had been used to draw 50,000,000 feet of wire 0.0108 inches in diameter, showed a wear of only 7/10,000 of an inch.

It may also be used for machining such hard materials as glass, which no metal tool has been able to cut.

Alloys. The chemist knows of 92 chemical elements. Most of these have been isolated in pure form and their properties studied, although a few are known only from spectroscopic or x-ray evidence and have never been obtained in anything like a pure condition. These elements unite with each other to form an enormous number of compounds, each with its own characteristics and uses. The studies of the types of compounds and of their properties as dependent on their constitution form the very core of the science of chemistry.

There exists, however, an infinite number of mixtures of elements and mixtures of compounds which are, properly speaking, not compounds themselves. Thus sand and sugar can be mixed in any proportion, the properties of the mix-

ture (density, color, etc.) depending on the percentage of each substance present. With a microscope it would be possible to ascertain that crystals of sugar exist in the mixture as separate entities and that the crystals of sand are still individuals. This kind of mixture is of a purely mechanical sort and could be made by grinding sugar and sand together in the proper type of mill.

If, now, we consider two metals, say copper and nickel, and make our mixture, not by grinding but by putting the two metals together and heating them till they are melted, we shall find when the mixture is cooled that we have a very nearly homogeneous mass. With a microscope we could not tell that two substances are present. This results from the fact that copper and nickel are soluble in each other, *even in the solid phase.* The properties of our mixture will not be the same as those of either pure nickel or pure copper and, but for chemical analysis and the fact that the melting point is not sharp, we might never suspect that we were dealing with a mixture. In still another case, say aluminum and zinc, we might detect different crystals with a microscope, depending on the percentages used. Some of the crystals might contain both aluminum and zinc and would be *solid solutions,* while still others might be pure zinc. The crystals may be so minute and the mixture so complete that the mixture as a whole may have very definite properties not at all resembling those of either pure zinc or of a solid solution.

These intimate mixtures of metals are sometimes referred to as alloys. They are of many different types and are, of course, infinite in number. Since a complete study of the possible mixtures of any two metals is rather laborious, relatively few systems have been studied with any thoroughness. With three or more metals in the mixture, a detailed study is a matter of years and decades. And yet some of the most interesting and important advances of modern industry depend on the use of alloys. Frequently the find-

ıg of an alloy for a particular purpose is a matter of hance, but, as more data accumulate, certain guiding rinciples become evident and systematic studies of certain ombinations of metals have produced fundamental results.

Permalloy and Perminvar. The telephone and radio inustries have need of alloys with very special properties. n order to understand these, we must first enter into a hort discussion of the field of magnetism.

Let us consider a magnetic field. The lines of force proeed from the north to the south pole. The greatest inensity of the field is on the line joining the center of the two oles. It may be said that the only line of force which is erfectly straight is the one which would join two poles of pposite sign by the shortest possible distance. Around this hortest line, the other lines of force spread out in a somehat semicircular fashion, so that the intensity of the ıagnetic field decreases as one proceeds in a direction at ight angles to the axis of the field.

Some substances, when placed between the poles of the ıagnet have the power of drawing in or concentrating the nes of force so that the intensity of the magnetic field beomes much greater through the body and the intensity utside becomes correspondingly weaker. These substances re called paramagnetic. Still other substances act in such way that the lines of force have less tendency to pass hrough them than through air (or more properly a vacuum). 'hese are called diamagnetic. The measure of the extent ɔ which a substance gathers in the lines of force is called he *permeability*.

In electric circuits which use transformers, telephone reeivers, etc., paramagnetic substances are of great imporance. In a transformer an alternating current passes through coil surrounding an iron core. Surrounding the first coil, r surrounding another part of the iron core (usually in the ɔrm of a loop) is another coil of wire. In the ordinary lternating current used in most cities, the direction of the

current changes 120 times a second for a 60 cycle current. As the current flows through the first coil, the iron is magnetized first in one direction and then in the other. The changing magnetic field then *induces* a current in the second coil of wire.

Hysteresis. For such a transformer to be efficient, the energy lost in magnetizing the iron first in one direction and then in the other must be small. In other words, the losses due to hysteresis must be reduced as far as possible. If a piece of iron is placed in a magnetic field, it is magnetized. As the strength of the field is increased, the magnetization of the iron increases, usually approaching a more or less constant value. As the magnetic field grows weaker, the magnetization of the iron grows less, but the iron acts as though it retains a part of its magnetism. If the direction of the magnetic field is reversed, the iron will be magnetized, eventually, in the opposite direction. As one proceeds around such a cycle, magnetizing the iron first in one direction and then in the other, a certain loss is encountered due to the fact that the iron does not lose its magnetism as fast as the field acting on it decreases in strength. This loss is referred to as a hysteresis loss.

Evidently it is advantageous to have iron of low hysteresis for building transformers and for making telegraph relays where a moving bar is actuated by a piece of iron magnetized by a pulsating current.

It has been recognized that iron shows lower hysteresis losses for small field strengths when it is in a mechanically hard condition than when it is well annealed. The purity of the iron is also of great importance in this regard and very nearly pure iron was formerly considered to be the best.

Of the common metals, those which are most pronouncedly ferromagnetic are iron, cobalt and nickel. Pure or nearly pure iron was considered to be the best for electromagnetic purposes, but during the past few years important studies of alloys of these three metals have shown

that some of them are far superior to either of the pure metals.

Of these alloys those known as *permalloys* have been shown to be of the greatest interest and importance. These alloys have been developed by the Bell Telephone Laboratories and thorough studies of the magnetic and electrical properties of a large number of iron-cobalt-nickel alloys have been made.

The term *permalloy* is used to include iron-nickel alloys containing more than approximately 30 per cent of nickel. The ternary alloys of constant permeability and low hysteresis loss are called *perminvars.*

The heat treatment of the alloys influences to a certain extent their properties. For telephone and radio work, a low hysteresis loss at low flux density is of great importance. The alloy containing 78.5 per cent nickel and 21.5 per cent iron seems to meet this requirement better than any other. In the iron-cobalt series a 50 per cent mixture seems to be the best. With the range of field strength encountered in submarine cables permalloy has 40 to 50 times the permeability of iron. The cables are *loaded* by surrounding them with a sheath of permalloy, thus overcoming many of the unfavorable transmission characteristics resulting from the electrical capacity of the circuit. This *loading* is also necessary in telephone lines and is accomplished by placing coils with permalloy cores at regular intervals in the lines. Permalloy coils occupy but a small fraction of the space necessary for coils with iron cores. Permalloys are also used in the manufacture of relays, audio transformers, telephone receivers, etc.

Illium. A steel bomb lined with platinum has been extensively used in determining the heat of combustion of coals and of other materials. The platinum lining was necessary to resist the action of nitric and sulfuric acids formed in the combustion.

The high cost of the platinum lining led Professor Parr,

about 20 years ago, to begin a search for some alloy which would resist the action of nitric and sulfuric acids and which might be used for the construction of bombs for calorimetric use.

The Chromel Alloy. In 1900, A. L. Marsh, in his senior year, withdrew from his course in chemistry at the University of Illinois and entered the employ of William Hoskins of Chicago. Metallic chromium as an industrial product had just become available and, at Hoskins's suggestion, Marsh was set to work to see what could be done in the way of the development of that metal as a constituent of an alloy. He went to the University of Wisconsin and worked in the electro-chemical laboratory of Professor Burgess. As a result, he developed the "chromel alloy," which consists of 79 parts of nickel, 20 of chromium and 1 of aluminum. This alloy has a considerable electrical resistance and may be heated to quite a high temperature before it begins to oxidize in the air. It has proved to be the most important alloy ever manufactured for use in the heating elements of electric toasters, electric ovens and the like. It was the most promising material which seemed available for the construction of an acid resistant calorimeter.

Alloy Experience. An order was placed with Marsh for the construction of a bomb of the chromel alloy, in 1910. After waiting for some time, a visit was made to the Hoskins Manufacturing Company in Detroit. Marsh exhibited the results of his efforts to cast a bomb. The results were altogether disappointing, as was shown by pouring water into one of the castings; the water flowed through the casting so freely as to suggest the properties of a sieve and Marsh said that after spending something over $100 in experiments he was inclined to ask to be released from further attempts in that direction. This was, of course, granted.

However, in discussing the problem with Marsh it was agreed that it might be possible to start with the chromel alloy as a base and modify it along lines which would re-

sult in a metal with better casting qualities. The problem would then shift from the field of electric resistivity and non-oxidation at high temperatures, to non-oxidation, or non-corrosion in contact with acids at ordinary temperatures, but with the added requirement of modifying the melting or solidifying temperature in such a way as to secure a sound casting, free from leakage under very high gas pressure. This, in brief, was the problem undertaken.

It may be of interest to note that the compounding of alloys was, at that time, and, indeed, still remains almost entirely a matter of "cut and try." A sort of chemical reasoning, however, was entered into along this line—the solubility of an element bears no relation to the solubility of its compounds. May it not be that two metals, when they alloy, enter into a sort of combination in which the solubility of the resulting alloy bears no relation to the solubility factor for the individual elements, and may it not also be true that within a certain range of ratios of these two constituents, a higher degree of resistivity may be found than is the case with other ratios of the same constituents?

For example, copper is very soluble in nitric acid: assuming that copper would alloy with the nickel and chromium of the chromel alloy, would it increase or decrease the solubility of that alloy? Copper would be the first element to think of in this connection because it would lower the melting point of the combination. A series of tests was organized in which the copper was varied over a wide range of percentages to see what the effect would be. The first melt was made on April 4, 1911. The furnace used for heating was a Hoskins Electric Furnace, using carbon resistor plates.
The Chromel composition:

Nickel, 79; chromium, 20; aluminum, 1,

was modified to:

Nickel, 79; chromium, 10; copper, 10; aluminum, 1.

Strangely enough, this combination proved to be slightly

more resistive to the 25 per cent nitric acid test than the original chromel alloy. Subsequently, the series was modified by introducing a lower amount of copper, that is 5 per cent, resulting in a greatly increased resistivity—approximately one hundred times more resistant than either the original chromel alloy or the alloy with 10 per cent of copper added.

It was now necessary to study the effect of a higher chromium ratio, and this in turn permitted a higher copper percentage, which has the advantage of improving the casting qualities—so that there seemed to be a new starting point with a ternary alloy base composed of:

Nickel, 70; chromium, 20; copper, 10.

This has a solubility factor of 0.023 per cent in 25 per cent nitric acid for twenty-four hours, as compared with 1.3 per cent for the original chromel alloy.

While the castings from this composition were greatly improved, they were still porous, and a somewhat similar series of tests was inaugurated for the purpose of determining the limit which might be used for manganese as an addition.

Here, again, a rather unusual result was obtained. Up to about 4 per cent of manganese, the high order of resistivity was retained, while the texture of the castings was greatly improved. Aluminum in small amounts—less than 2 per cent—was also tried, but its function seemed to be mainly that of a scavenger. A complete non-porosity of the castings was still to be obtained.

At this point, in an effort to increase the density and at the same time, add a highly resistive element, the addition of tungsten was tried. Such a melt, No. 21, was made on October 1, 1911, and resulted in the first perfect casting obtained. This casting was in the form of a bomb cover and a composition calculated to the total make-up of the metal added, as follows:

Ni	65.2
Cr	18.6
Cu	9.3
W	3.7
Mn	1.6
Al	1.6

This cover was found to machine readily, was finished as a bomb cover and was at once put into service, where it has continued up to the present time.

While the casting of a cover had its pronounced difficulties, the attempt to cast a bomb was an even more serious problem. For a number of melts, therefore, slight variations in the composition were attempted, the chief modification being the addition of small percentages of scavenging constituents, such as silicon and boron. Of these, a part of the silicon remained as a constituent of the alloy.

In December, 1911, the first successful bomb casting was secured, the melt being No. 40. This casting was finished, being easily machined, and, when put into service, showed only one small pinhole about midway on the side of the bomb. This pinhole was readily soldered tight on the outside and the bomb was put into commission. It has been in continuous service since that date.

With the accomplishment of these two castings, one for a cover and one for the bomb proper, it was thought that the problem had been substantially solved. Solubility factors were obtained for 25 per cent nitric acid and also in a mixture of nitric and sulfuric acid of the same strength, the solubility being 2.16 mg. per square cm. for twenty-four hours in the mixed acids.

It was now supposed to be possible to reproduce these castings at will. A paper was prepared for presentation at the Eighth International Congress of Applied Chemistry, held in New York in the summer of the year following,

1912. The titles of the papers presented were: "A new alloy with acid resisting properties," "A new calorimeter bomb with special advantages as to material of construction and method of operation"; "Some tests on a new calorimeter bomb."

The strange part of the story now enters. In spite of every effort to reproduce this one successful bomb, no perfectly sound casting was obtained until April 23, 1913, the melt number being 96. Between melts Nos. 40 and 96, almost every conceivable experiment was made to secure sound castings. The resistivity of the metal was satisfactory; much attention was given to the core material and the baking of the cores, also to the use of green sand in the moulds, dry moulds and moulds of metal. The composition was modified, also, insofar as the use of tungsten was concerned, it being desirable to ascertain to what extent molybdenum would replace tungsten. The use of a high percentage of tungsten seemed to result in greater hardness and greater time required in machining. Melt No. 96 gave a perfect bomb, with molybdenum completely replacing the tungsten, but it was not until No. 99, obtained in June, 1913, that the experiments on composition seemed to have reached a satisfactory stage, so far as both casting and resistivity were concerned. In fact, melt No. 92, which, however, was poured into a cover casting only, seemed to furnish the key for the composition of subsequent melts and was substantially the one used in melt No. 99. This composition has undergone very slight modification in all the succeeding years and is shown substantially as follows:

Ni	60
Cr	24
Cu	8
Mo	4
W	2
Mn	1
Si and other elements	1

It may be a little difficult to understand why all the failure and grief should accompany the development of this seemingly simple proposition. As a matter of fact, it was not until July, 1915, in melt No. 134, and for the following six numbers that anything like consistent results were obtained. In this series of melts, there was only one bomb failure and the solubility tests for twenty-four hours in 25 per cent nitric acid showed throughout a "0" solubility.

In fact, the record of one of these bombs in use by the Commercial Testing and Engineering Laboratory of Chicago, shows at the present time a perfectly bright and polished surface, both inside and out, after more than 50, 000 determinations, mostly on Illinois coal, where the high sulfur content results in a very positive mixture of sulfuric and nitric acids in connection with the combustions for calorimetric determinations.

The fact has been well established that in the final method adopted the conditions to be used are very exacting with regard to minor factors of composition, the scavenging effect of small constituents used for that purpose, the temperature of pouring, the physical condition as to porosity, moisture content, venting, etc. of the moulds. It required substantially steady experimentation on these various points for almost the entire period of intervening years since the inception of the first experiments, before a stabilized procedure was established.

The melting point of the metal is about 1260°C. For special castings, however, the metal requires a superheat of at least 300°C. The metal is hot short until a temperature of about 1000°C has been reached in cooling. These conditions require special construction in the making of patterns; special provision for cooling in the mould from one point only, rather than from a number of points, in order to avoid shrinkage cracks; and, in fact, a special system of foundry practice had to be worked out.

The metal has been rolled into sheets and drawn into

wire, but only in small amounts. The working temperature is below 600°C. and the metal is too hard at that temperature to make rolling into sheets industrially practicable. The tensile strength of the cast metal is above 70,000 lbs. per square inch. It machines readily and takes a high polish, which it retains indefinitely. The specific gravity is 8.7 and the Brinnel hardness is less than 200.

It is a standard practice to pour two test pieces from each melt, which, after being cleaned and shaped, have approximately two square inches of surface. One sample is placed in 25 per cent sulfuric acid and the other in 25 per cent nitric acid and the two are kept at the boiling temperature for twenty-four hours. The loss in weight should not exceed two or three milligrams per square centimeter, which, under similar conditions as to acid and heat would indicate a penetration due to solubility of approximately 0.03 inch in a year. Tests of this sort are, of course, comparative only with reference to the metal itself, but they serve as a good method for indicating whether the material is up to grade.

At the present time the use of the metal has extended far beyond its original purpose in connection with the construction of calorimetric apparatus. It is used extensively in the manufacture of acid pumps of several standard designs, of acid valves and fittings, in the construction of various types of machinery used in the chemical industries, in nuts, bolts and washers, in the tie-bolts for the assembling of pickling vats, for capsules and crucibles in coal analyses, for certain parts of the mechanical features involved in the rayon industry, etc. It is not uncommon, at the present time, to pour an amount of metal aggregating a ton of this material per week, and its use is steadily on the increase.

References

Hevesy, G. "Discovery of hafnium." *Chem. Rev.*, 1925, **2**, 1–41.

HEVESY, G. "The use of x-rays for the discovery of new elements." *Chem. Rev.*, 1927, **3**, 321–329.

NODDACK, TAKE, and BERG. "Discovery of masurium and rhenium." *Naturwiss.*, 1925, **13**, 567.

NODDACK, IDA and WALTER. "Preparation and properties of rhenium." *Ztschr. f. phys. Chem.*, 1927, **125**, 264.

C. C. KIESS. *Spectral lines of No. 61.* Bureau of Standards Scientific Papers, Nos. 421, 442, 466 (1928).

YNTEMA, L. F. "Spectral lines of No. 61 in violet." *Jour. Am. Chem. Soc.*, 1924, **46**, 37; 1926, **48**, 1585.

HARRIS, J. A., and B. S. HOPKINS. "Discovery of illinium." *Jour. Am. Chem. Soc.*, 1926, **48**, 1585.

HARRIS, J. A., L. F. YNTEMA, and B. S. HOPKINS. "Discovery of illinium." *Jour. Am. Chem. Soc.*, 1926, **48**, 1594.

JAMES, C. "The use of bromates for separating rare earths." *Jour. Am. Chem. Soc.*, 1908, **30**, 182.

CORK, J. M., C. JAMES, and H. C. FOGG. "Concentration and identification of element No. 61." *Proc. Nat. Acad.*, 1926, **12**, 696.

MEYER, R. J., G. SCHUMACHER, and A. KOWTOWSKI. "Element No. 61 (illinium)." *Naturwiss.*, 1926, **14**, 771–772.

ROLLA, L., and L. FERNANDES. "Florentium." *Gaz. chim. ital.*, 1926, **56**, 435–436.

ROLLA, L., and L. FERNANDES. "Florentium." *Ztschr. anorg. allgem. Chem.*, 1926, **157**, 371–381; 1927, **160**, 190–192.

PAPISH, JACOB, and EUGENE WAINER. "Element No. 87." *Jour. Am. Chem. Soc.*, 1931, **53**, 3818.

ALLISON, FRED, and E. J. MURPHY. "Elements Nos. 85 and 87." *Phys. Rev.*, 1930, **35**, 285; *Jour. Am. Chem. Soc.*, 1930, **52**, 3805.

WASHBURN, E. W. "Estimating atomic weights with the aid of the periodic law." *Jour. Am. Chem. Soc.*, 1926, **48**, 2351.

BALKE, C. W., and EDGAR F. SMITH. "Atomic weight of columbium." *Jour. Am. Chem. Soc.*, 1908, **30**, 1637–1668.

SMITH, EDGAR F., and W. K. VAN HAAGEN. "Atomic weight of columbium." *Jour. Am. Chem. Soc.*, 1915, **37**, 1788–1797.

BALKE, C. W. "Ductile tantalum." *Ind. and Eng. Chem.*, 1923, **15**, 560.

BALKE, C. W. "Metals of the tungsten and tantalum groups." *Ind. and Eng. Chem.*, 1929, **21**, 1002.

FORSTER, R. "The space lattice of permalloy." *Physik. Ztschr.*, 1926, **27**, 829–830.

McKEEHAN, L. W. "Atomic groupings in permalloy." *Jour. Franklin Inst.*, 1927, **204**, 501–524.

ELMEN, G. W. "Magnetic properties of perminvar." *Jour. Franklin Inst.*, 1928, **206**, 317–338.

PARR, S. W. "A new calorimeter bomb." *Jour. Ind. Eng. Chem.*, 1912, **4**, 746–748.

JESSE, R. H. "Tests on a new calorimeter bomb." *Jour. Ind. Eng. Chem.*, 1912, **4**, 748–749.

PARR, S. W. "An acid resisting alloy." *Jour. Am. Chem. Soc.*, 1915, **37**, 2515–22.

Chapter VII

THE ELIXIR OF LIFE

The alchemists sought the Philosopher's Stone for a thousand years. This Stone, when found, was to transmute the baser metals into gold. Several centuries after that quest had been given up as hopeless, and in quite recent times, it has been discovered that certain elements actually undergo a spontaneous transmutation and some chemists have even thought that they had changed mercury into gold. Such a transmutation is no longer considered impossible or absurd. These transmutations were not discovered by a direct search for the Philosopher's Stone, but as the result of years of patient work by men and women who were seeking, primarily, a better knowledge of the universe about us.

The alchemists thought that the Stone, when found, would not only transmute base metals but that it would cure all diseases and give to its fortunate possessor, eternal youth. Such an Elixir of Life has not been found, but methods for the almost complete control of some diseases have been found and other diseases have been nearly eliminated from the world. As with transmutation, the foundation for the successes so far obtained rests on an intensive study of the character of minute organisms, which are the cause of many diseases, and of the processes which go on in the human body. Marvelous and encouraging as are the achievements of the last seventy-five years, one who reads the story in detail must be impressed with the profundity of our ignorance about some of the most fundamental problems still to be solved.

I. Medicine as an Art

Until comparatively recent times, medicine was an art rather than a science. It was very much in the condition of the cotton seed oil industry before it established laboratories and employed trained men. I once heard a chemist say that the manufacturers were "chuck-full of theories" but they could not produce a uniform product. They had many ideas derived from "practical" experience, not accurately controlled. That is the condition of nearly all "arts" so long as they are in the hands of men who are not thoroughly imbued with scientific methods of thought—and in so complex an art as medicine even our best physicians must continue to practice the *art* for a long time to come. An "art" cannot wait for accurate scientific knowledge to guide it, but must guess to the best of its ability. The conditions which we call disease are so varied, and the relations between the remedies used and the results obtained are so obscure and so difficult to follow, that it is not surprising that many of the older guesses were very wide of the mark and we are quite inclined to think that more patients were killed than were cured by the physicians of the middle ages. There was an early and very persistent opinion that diseases were caused by supernatural agencies, and this opinion, combined with erroneous ideas derived from imperfect observations, caused the progress of medicine toward rational and successful practice to be very slow.

Hippocrates, the Greek physician, who lived four centuries before Christ, made many surprisingly keen observations about the symptoms of disease and knew a good deal about the proper treatment of dislocations and fractures. His ideas about the causes of disease partook, however, of the crude philosophy of his times. He accepted the doctrine of the four elements and connected the properties of these so-called elements with the various "humors" of the body. He considered that the blood represents "warmth"; mucus, "cold"; yellow bile, "dryness"; and black bile,

"moisture." Diseases were supposed to be due to something wrong with one or more of these fluids or "humors." It is evident that only a small beginning of a science of medicine could be built on such a basis.

Nearly six hundred years later, Galen revived many of the doctrines of Hippocrates and made such an impression on the physicians who followed him that he was considered the greatest authority in medicine for a dozen centuries. Drugs are still sometimes called, after his name, "galenicals." He made many correct observations and used a considerable number of drugs with discrimination.

II. Medical Chemistry

When the alchemists began to give up the transmutation of metals and the search for the elixir of life as idle dreams, some of them turned to chemistry as the handmaid of medicine and sought substances which might be used in the art of healing. One of the first of this school was Paracelsus, who lived in the beginning of the sixteenth century. His full name was Phillipus Theophrastus Aureolus Paracelsus Bombast von Hohenheim. Until the etymology of "bombast" is looked up one might think the word came from his name, but this is not the case. He made few additions of value to medical practice, but he helped the physicians of his day to free themselves from that servile acceptance of authority which prevents individual initiative and is so fatal to progress. In recognition of this service, and of his attitude which raised the healing art to the level of a religion, a Paracelsus-Gesellschaft has been founded in Munich. In their prospectus, they emphasize the ferment of the Renaissance as similar to the way in which men today are reaching out for something new and better than the past.

Another man of the age of medical chemistry is Basil Valentine, who wrote a treatise on "The Triumphal Car of Antimony." There is a story of him which will bear repeating, though it is almost surely apochryphal. It is said that

he tried out various preparations of antimony on monks, sometimes with disastrous results—hence the name, antimony. It is not likely that his use of antimony cured many patients. It is worth while to contrast the rough, uncertain methods, which were the only ones possible in his day, with the methods of Pasteur, Behring, Ehrlich, Kendall, Adams and others in recent times.

III. Smallpox

Edward Jenner, a contemporary of Washington, was the first to place immunity on a scientific basis. During the eighteenth century and before, epidemics of smallpox swept over Europe, taking a toll of hundreds of thousands of lives. Inoculation with the disease was sometimes practiced, but this was often fatal to the patient and did not come into general use. Jenner studied medicine with John Hunter, as an apprentice, according to the common practice of that time. Sometime after he had begun to practice by himself, he wrote to Hunter saying that he had observed that milkmaids who had contracted cowpox were immune to smallpox and that he thought it possible to secure acquired immunity in this way, on a large scale. Hunter replied, "Do not *think*, try; be patient; be accurate." Following this, Jenner continued his observations for eight years before he performed his first vaccination. Two years later he published an account of his work and from that time vaccination gradually made its way into general favor and today smallpox has practically disappeared from communities where it is rigidly enforced. It would be interesting to know how much this single step toward the conquest of disease has contributed to the rapid growth of population in Europe during the nineteenth century. The English Parliament gave Jenner a grant of 20,000 pounds with which to carry on his experiments.

There can be little or no doubt that smallpox is caused by some specific virus, but this has not been satisfactorily

demonstrated and our knowledge of the cause of the immunity resulting from vaccination is almost as indefinite as it was in the time of Jenner. An intelligent search for similar methods to be applied in the war on other diseases had to wait for the demonstration of the relation of diseases to the living organisms which caused many of them.

IV. Louis Pasteur

In 1822 there was born in Dole, France, a man who has contributed more than any other to place preventive medicine on a scientific basis. It is much to the credit of the French people that in a popular vote taken some years ago they called Louis Pasteur, and not Napoleon or Victor Hugo, the greatest Frenchman.

As chemists, we have some reason to be proud of the fact that Pasteur was trained as a chemist and that his first notable discovery was the separation of racemic acid into its optical antipodes, a discovery which required an intimate knowledge of chemistry, crystallography and physics.

In 1854 Pasteur was appointed Professor and Dean of the Faculty at Lille. Soon after, the father of one of his students consulted him about his difficulties in carrying out the fermentation of his wines. The fermentation went wrong at times without any apparent reason. At that time the whole question of the cause of alcoholic fermentation was in a very confused condition. Berzelius and Liebig, the greatest chemists of the time, believed that fermentation was caused by decomposing organic matter acting by its presence, catalytically. It had been noticed, of course, that yeast is present and increases in amount during the fermentation, but Liebig and Berzelius considered its presence accidental and not the cause of the fermentation. By a series of brilliant experiments Pasteur demonstrated that the alcoholic and lactic fermentations are caused by two different organisms and that these organisms may be cultivated in solutions containing only inorganic compounds in addition to the sugar.

His work was carried out with such care in all its details that even the authority of Liebig could not prevent the acceptance of his conclusions.

In his papers of this period, Pasteur stated that the organisms which cause both the alcoholic and lactic fermentations appeared "spontaneously" in liquids containing materials suitable for their growth. He added, however, that he used the word "spontaneous" only as a statement of fact and that he expressly reserved the expression of any opinion on the question of "spontaneous generation." It is evident that the discovery that the organisms producing the two kinds of fermentation are different and distinct in their characteristics was already preparing him to understand that the organisms did not originate, *de novo,* under the conditions of his experiments.

V. Spontaneous Generation

A study of this fundamental problem next engaged his attention. From the earliest times spontaneous generation was almost universally taken for granted. Even van Helmont, a contemporary of Shakespeare, wrote that if one puts away some soiled linen and some wheat in a dish and leaves them for a few days, "the odor of the linen and that of the wheat will combine and the grain will transform itself into mice, not little ones but full size and running about." While no one would have accepted such a story as this when Pasteur began his work, the thought of the time was favorable to the idea of spontaneous generation and several observers believed that they had demonstrated its occurrence. At that time atheists, agnostics and materialists ranged themselves, instinctively, on the side of spontaneous generation, while believers in the church and in revealed religion were, many of them, passionate in their denial of its possibility. Pasteur, who held a simple religious faith, raised himself far above such partisanship. To him, it was simply a question of *fact* and he was equally ready to accept evi-

dence for or against the beginning of *new* life. His friends advised him very strongly against undertaking experiments on such a difficult subject but, with the spirit of a great man, the very difficulties inspired him.

It is interesting to notice that each of his studies followed in intimate relation with his previous work—a characteristic of nearly all scientific research. The inquiry of the wine merchant seems accidental, but, as Pasteur himself delighted in saying, such accidents come only to those who are ready to profit by them. In his study of racemic acid, he had found that a certain organism will destroy the right-handed tartaric acid and leave intact the left-handed form—as Emil Fischer said many years later, "the little bugs have a better appetite for the right-handed molecules than for the others." This led Pasteur to think that optical activity of natural compounds must always be associated with life and that the active amyl alcohol found in fermented liquids must be due to the action of organisms. His ideas in this case were only partially true but they led him in the right direction, to his successful studies of fermentation. These studies, in turn, led him to the discovery that spores of yeast are very prevalent in the air and this, again, to a search in the dust of the air for the organisms which cause fermentation, putrefaction and decay.

Starting with this fundamental thought, Pasteur devised a series of ingenious and convincing experiments. He prepared a large number of flasks containing solutions of organic compounds, sugar and other substances, which would ferment and change very rapidly on the addition of some of the organisms found in the air. He drew out the necks of some of these flasks into a long narrow, sinuous form and boiled the solutions to sterilize them. On allowing the flask to cool slowly, the air drawn in through the open neck deposited its dust in the narrow tube and the solution kept indefinitely without any sign of life. If he sealed the end and broke the tip after the solution had become cold, the sudden rush of

air carried the dust through the tube and the liquid fermented.

In many other experiments he broke the tips of prepared flasks in various places to determine whether the germs are always present in the air. When the tips were broken in the cool, still cellar of the observatory, the liquid fermented in only one of the six flasks he tried; when the tips were broken in the court of the observatory, the liquid fermented in every one of a dozen flasks; of twenty opened on the Mer de Glace, nineteen remained sterile. Very many other well-designed experiments were tried, and since that time it is only prejudiced men who have been so hardy as to maintain that spontaneous generation has ever been actually observed. The doctrine that living things are never found otherwise than as descended from other living things is as much an axiom on which all modern bacteriology rests as the doctrine of the non-transmutation of the elements was an axiom to the chemists of thirty years ago. Very few scientific men would dare say that this will always be true but no one is justified, at present, in basing his philosophy on the assumption of spontaneous generation. We can only say of the origin of life, "We do not know."

At the close of his communications on spontaneous generation, Pasteur made the remark that the best side of these investigations was that they would lead the way to a serious study of the causes of disease. These were the words of a prophet who had a clear vision of whither his work was leading him.

Surgery. The first important application of Pasteur's discoveries in the surgical treatment of human beings was made by Joseph Lister in Glasgow. Before that time, seventy per cent of compound fractures were fatal because of the contamination of the wound with bacteria, causing the death of the patient. Amputations were fatal in half of the cases. I have heard Dr. Keen of Philadelphia speak very feelingly of the "dirty surgery" he and others practiced, in

ignorance, during our civil war, resulting in the death of thousands of brave men whose lives might have been saved by modern, antiseptic or aseptic surgery. In 1874, after his antiseptic methods of surgery had been in successful use for some years, Lister wrote a letter to Pasteur saying that Pasteur's brilliant researches had demonstrated to him the truth of the theory of germs of putrefaction and that it was this single principle which had given him his success.

Since then, surgery has made further advances in several directions; in better aseptic methods, such as the sterilization of instruments and the personnel of the operating room; in better sterilizing solutions, especially Dakin's solution of neutral sodium hypochlorite, and several chloroamines; and in the use of an antitoxin for tetanus when a wound has been accidentally infected. Some of these will be mentioned further on.

Anthrax. Some time later Pasteur undertook a study of anthrax. In this work, he developed a vaccine for anthrax which imparted a mild form of the disease. After vaccination a second time with a somewhat more virulent organism, sheep and cattle became immune. The veterinarians of the time would not believe such revolutionary doctrines and Pasteur was challenged to a spectacular contest. Fifty sheep were selected. He treated twenty-five of these with his vaccines. After the proper time, the whole fifty were inoculated with virulent anthrax. The twenty-five which had been vaccinated remained well; the other twenty-five died.

Jenner's discovery of vaccination for smallpox must be considered as a happy, accidental observation followed out with painstaking care. Pasteur's discovery of vaccination for anthrax was the result of carefully planned experiments, with a vivid imagination which led him to see a possible success.

Hydrophobia. He next turned his attention toward the development of a method of rescuing persons bitten by a mad dog. This problem was much more difficult. After five years of experimentation, he discovered how the organism

which causes hydrophobia could be attenuated in different degrees and how, by a series of inocculations with viruses of increasing activity, immunity from the development of the disease could be secured, even after an individual had been bitten. After his method had been developed and had proved successful with dogs, a boy who had been bitten on the face and elsewhere by a mad dog, was brought to his laboratory. Pasteur knew, when he saw the boy, that he would certainly die in terrible agony if he could not be rescued by his treatment. He had not yet tried the method with a human being and he debated with himself, with great anxiety, whether he should make the trial. A failure would, perhaps, postpone indefinitely the successful treatment of other cases. Considerations of humanity finally prevailed and he carried through the series of inoculations with entire success. Since then, the lives of thousands have been saved by the Pasteur treatment and the world has been relieved of one of its greatest horrors.

V. Immunity

The studies of immunity since these early discoveries of Pasteur have left us still very much in the dark as to the nature of the poisons produced by bacteria and the actual cause of immunity. They have given us a number of practical and very valuable methods for combating a comparatively small number of diseases, but very little is known about the chemical character of the toxins or how they are neutralized by the antitoxins.

The following is a brief summary of some of the most important facts:

1. In our skin there are glands which elaborate an oily secretion, composed largely of esters of cholesterol, which partially waterproof the skin and help to make it impervious to bacteria. Our skin is almost constantly in contact with germs which would kill us if any number of them found their way into the blood.

2. The gastric juice of the stomach contains hydrochloric acid in sufficient concentration to kill or injure most of the bacteria which might attack the animal body.

3. When the skin is broken by a wound, if the wound bleeds, the dangerous bacteria are partly washed away and partly killed by the white corpuscles of the blood, called leucocytes. If the blood stream is invaded, the number of leucocytes increases rapidly in the war between the human organism and the threatened danger. A determination of this increase by examining the blood is one means for the diagnosis of appendicitis.

4. When the bacillus which causes diphtheria attacks the throat, or the one which causes typhoid fever attacks the intestines, the organism in some way develops a specific "antitoxin." The chemical nature of these antitoxins is not at all understood but it seems that they may act in two ways; they may kill the bacteria or prevent them from multiplying so far as to produce the disease; or they may combine with the toxin or poisonous substance produced by the bacteria. These antitoxins may accumulate in the blood serum of a horse, goat or other animal which is inoculated with the bacteria which cause the disease and the serum from such a source may be used to produce immunity or to alleviate the disease after it has been acquired. This method was first developed by Behring for diphtheria. Since then, one of the most dreaded and fatal diseases has been brought largely under control.

Typhoid. A variety of methods have been used for the control of typhoid fever. Soon after it was understood that the disease is often carried in drinking water, some cities introduced means for the control of their water supplies but thousands of people died in Chicago and many others had long serious illnesses before the drainage canal and the extension of the intake gave the water a comparative purity. Now the water supply of all large cities is very carefully controlled and the water is sterilized with chlorine when

better methods are not available. The supply of pure water has not, however, prevented serious epidemics of typhoid from milk and other sources. A serious menace has arisen, occasionally, from "typhoid carriers"—persons who have had typhoid and are, themselves, immune but who continue to harbor typhoid bacilli in their persons. In spite of knowledge which should have prevented such a catastrophe, thousands of our soldiers died from typhoid during the Spanish-American war. For the Great War all our soldiers were treated with typhoid vaccine and the number of deaths from typhoid was negligible. The disease can now be prevented, if proper means are used.

Not all diseases can be prevented or cured by means of antitoxins. Fortunately, there are many other methods of prevention and cure. Some of these were discovered empirically, while medicine was still an art and had very little scientific knowledge to guide it. The Indians of Peru discovered that cinchona bark is a specific for malaria. The Spaniards learned this from the Indians and after 1640 the bark made its way very slowly into European medical practice. It could not be accurately and satisfactorily used, however, until Pelletier and Coventou, in 1820, isolated quinine from the bark. It is now pretty well established that quinine has a selective action on the proteins of the organisms which cause malaria and that enough of the drug may be administered to kill completely these pernicious organisms without seriously injuring the patient. It should not be forgotten, however, that quinine is poisonous to human protoplasm, also.

Malaria and Yellow Fever. While the discovery that the organism which causes malaria may be killed after it has invaded our bodies is very valuable, still more important discoveries have been made since the life history of the organism and the way in which it enters the blood have been established. Malaria is not contagious as smallpox and measles are. The malarial organism has a dual life, partly in

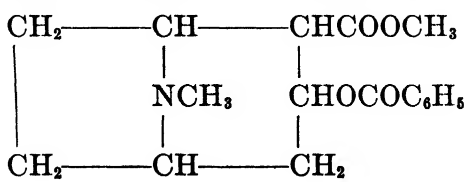
the body of mosquitoes of a definite and well known species, partly in the body of an individual who has acquired the disease from the bite of such a mosquito. This cycle can be stopped either by the complete elimination of persons who have the disease or by the destruction of the mosquitoes. These two methods more or less supplement each other but the second method is evidently best for quick and effective control. It was the method used by Gorgas in the Panama Canal Zone, to suppress both malaria and yellow fever. Without it the French failed in their efforts to build the canal and without it Americans would have failed, also. The control is effected by draining areas where stagnant water accumulates and furnishes a place for the growth of the larvae of the mosquitoes, or by covering water where mosquitoes breed with oil, or dusting over it Paris Green or some chemical which will kill the larvae.

When an individual has acquired yellow fever, curative medicine is, at present, almost entirely helpless. The life history of the organism which causes the disease is even more complicated than that of the malarial organism. The disease is transmitted by means of a different species of mosquito and the organism must live in the body of the mosquito for a number of days before the bite of the mosquito will communicate the disease. This was finally demonstrated in Cuba by means of soldiers who volunteered for the experiments and some of whom died. These soldiers were certainly among the greatest heroes of modern times and they have been so honored by our government. More recently, Noguchi, the great Japanese bacteriologist, has lost his life while working on the problem of yellow fever in Africa, and Paul A. Lewis of the Rockefeller Institute has died in the same way in Brazil. The disease, which once took a toll of thousands of lives in the United States, and which was long endemic in Havana and in other places in tropical America, has now been almost completely eliminated from the Western Hemisphere.

Anesthetics. Chemistry has furnished surgeons with several substances which may be used to render patients insensible to pain during an operation. The most important of these are ether, chloroform, nitrous oxide, nitrous oxide and oxygen, and ethylene and oxygen. With the aid of these, the surgeon may perform his delicate operations quietly and patients are relieved of a vast deal of suffering.

The value of anesthetics is not confined, however, to its use in operations on human beings. They are used, almost daily, in biological laboratories for operations on animals and without their use it would have been impossible to secure much of the information which has changed many kinds of medical treatment from mere guess-work to a scientific basis, with good assurance of success. It is difficult to understand how anyone familiar with the results obtained by such experiments can consider the alleviation of human misery as unimportant in comparison with the death of animals.

Local Anesthesia. In 1884 Koller of Vienna used cocaine to produce a local anesthesia of the eye as a preparation for a surgical operation. This soon led to its use for the extraction of teeth and other purposes. Unfortunately, cocaine is quite toxic and its use caused occasional deaths. It is also a habit-forming drug and there is serious danger in its use, for that reason. Further, its solutions are unstable. No better natural compound has been discovered for the production of local anesthesia. As a preparation for the discovery of other compounds which might be used in place of cocaine, it was necessary to determine the structure of the alkaloid. This difficult problem was finally solved by Merling, Einhorn, Ladenburg, Willstätter and others. The structure is,



When the structure was known, systematic experiments were undertaken to discover which part of the molecule is responsible for the anesthetic effect. It was found that compounds with a far less complicated structure produce such effects and that the benzoyl group, C_6H_5COO—, seems to be the most important fraction of the structure of cocaine. After the preparation of a large number of compounds, eucaine, stovaine, alypin and novocaine were obtained in Germany before 1905. The last of these, under the name of procaine, $NH_2C_6H_4CO_2CH_2CH_2N(C_2H_5)_2HCl$, was the best of this earlier series. The addition of epinephrine (adrenaline) decreases its toxicity, which is much less than that of cocaine, increases the duration of the anesthesia and decreases hemorrhage. During the World War, procaine was designated by the committee on synthetic drugs of the National Research Council as one of the three most valuable and indispensable drugs. Since that time it has been manufactured in America at a low cost and of an excellent quality. Procaine must be injected hypodermically to produce its effect and lacks the effect of anesthesia by surface application, characteristic of cocaine.

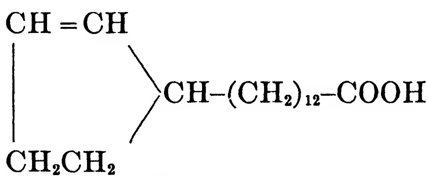
The manufacture of acetone by a fermentation process, during the war, gave quantities of normal butyl alcohol as a by-product. Trimethylene glycol had been a by-product of the manufacture of glycerol from rancid fats. Using these compounds and other well-known substances, Adams and Kamm succeeded in preparing another useful local anesthetic, butyn, which has the structure, $(NH_2\langle\equiv\rangle COOCH_2CH_2CH_2N(C_4H_9)_2)_2\ H_2SO_4$. This was discovered after preparing a series of other compounds, of greatly varying anesthetic effect.

The discovery of eucaine, procaine, butyn and other new local anesthetics illustrates a quite new method of finding useful therapeutic agents. The determination of the structure of some compound obtained from natural sources is made the starting point for the synthesis of hundreds of

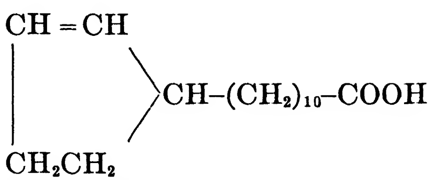
other compounds of related structure. Each of these compounds is tested for its physiological or bactericidal effects and for the relation between such effects and changes in the groups present in the compounds prepared.

Leprosy is a scourge which has caused untold suffering from very early times. Until recently the only hope of controlling the disease has been the segregation of those afflicted with it and the prevention of its spread by contagion. For some centuries it has been known that treatment with chaulmoogra oil is beneficial and will sometimes produce a cure. Not till 1899 was any attempt made to study the oil from a medical or chemical standpoint. Dr. Power and his associates in the Burroughs-Welcome laboratory in London isolated chaulmoogric and hydnocarpic acids from the oil. Because these two acids had not been found previously in any of the common oils, they were assumed to be the effective agents against leprosy. Walker and Sweeney, in 1920, confirmed this assumption by bactericidal tests.

The structures of these acids are:



Chaulmoogric acid



Hydnocarpic acid

These acids are present in the natural oil as glycerides, which are very viscous. The earlier steps in improved treat-

ment consisted in mixing less viscous oils, as olive oil, with the chaulmoogra oil, to cut down the viscosity. Later the acids of the oil were converted into sodium or potassium salts which could be injected intravenously to better advantage. The ethyl esters of the acids have also been used, as they have the property of being much less viscous than the natural oils.

For some years Roger Adams and his associates have been preparing synthetic products related to chaulmoogric acid in the hope of finding something effective to take the place of the natural compound. They used as the basis for their investigations information obtained from a study of pure chaulmoogric acid and some of its derivatives. Chaulmoogric acid was selected in preference to its homologue, hydnocarpic acid, because the former is more easily obtained.

The general program followed was to modify the chaulmoogric acid molecule at different points and test the new compounds prepared, bactericidally, *in vitro*. They eliminated, first, the olefinic linkage and tested the product. They then prepared a compound in which the carboxyl group, COOH, was replaced by the group $CH_2N(C_2H_5)_2$. Both of the compounds showed bactericidal properties and it was concluded that the essential factor in the molecule is the ring structure, since stearic and palmitic acids, which are analogous acids without ring structure, are entirely non-bactericidal when tested under the same conditions.

The synthetic program was then continued by preparing derivatives of cyclohexyl, which contains a ring of six carbon atoms and is much more easily available than other ring structures. The carboxyl was left at the end and it was found that the maximum effect was obtained in a molecule of 15 to 18 carbon atoms. Longer or shorter side chains than 9 to 12 carbon atoms were less effective and, with side chains of 7 or 14 carbon atoms, the bactericidal property was almost gone.

The next problem was to compare these cyclohexyl acids

with isomers having the carboxyl at different positions in the chain, especially near the cyclohexyl group. This work was undertaken with the idea that if these latter compounds were just as satisfactory, the synthetic work would be tremendously simplified and much more rapid progress could be made. The isomeric compounds with the carboxyl group near the ring were actually more bactericidal than with the group at the end of the chain.

Various ring structures were then studied and it was found that in every instance, with rings of 6, 5, 4, or 3 carbon atoms and the carboxyl on the 1st, 2nd, 3rd or 4th carbon atom from the ring, there was essentially the same bactericidal action with compounds of the same molecular weight.

Since, chemically, these various acids with different rings were quite different from one another, it was immediately concluded that it is far more probable that the bactericidal action is due to a combination of physical properties and not to specific chemical properties. As a consequence, they felt fairly safe in concluding that the original hypothesis that a ring is necessary is probably incorrect. Acids in which the carboyxl was moved from the end of a straight chain toward the middle were next studied. In acids of proper molecular weight, bactericidal action appeared and the property increased slightly as the carboxyl was moved toward the middle of the chain. It was found that the bactericidal effects are essentially of the same order as those of acids with a ring, provided the molecule contains 15 to 18 carbon atoms.

Recently a very extensive study of the surface tension effects of these acids has been made and all of those acids with the greatest bactericidal action also have a large effect on lowering the surface tension. Of course it does not follow that anything that would lower the surface tension would be bactericidal.

Between 180 and 200 acids have been prepared and tested

bactericidally, *in vitro*. One of these, di-n-heptyl acetic acid,

$$\left.\begin{array}{l} CH_3CH_2CH_2CH_2CH_2CH_2 \\ CH_3CH_2CH_2CH_2CH_2CH_2 \end{array}\right\rangle CH-COOH,$$

has been selected for clinical tests and the ethyl ester of this acid as well as the sodium salt, glycollide and glyceride have been shipped to the Philippines for trial with lepers there.

Pernicious anemia was first clearly described by Combe, a Scotch physician, about a century ago. Until quite recently arsenic and iron were the remedies most used for the disease and these gave such indifferent results that the malady was frequently fatal and was thought of as incurable.

About ten years ago, a study of the Periodic Table by Hammett and his co-workers led to the suggestion that compounds of germanium, which is next to arsenic in atomic number, might be useful in the treatment of anemia. They used germanium oxide, and their studies and those of others have shown the beneficial effects of germanium compounds in cases of severe anemia.

Much more recently, Minot and Murphy have introduced the use of liver in the diet and have found this very helpful. Liver had been used for many years before this time by the natives of Ceylon as a mode of treatment for sprue, a tropical disease closely resembling pernicious anemia.

Still more recently, an active principle has been prepared from liver and this may be used instead of the liver, of which large quantities were required to be effective. It has also been found that a preparation of desiccated hog's stomach is effective in causing an increase in the red cells of the blood, which are seriously depleted in anemia.

For several years past, Dr. Rosalie M. Parr, of the University of Illinois, has furnished physicians in Peoria, Chicago and Champaign, Illinois, in Claremont, California, and in Minneapolis a preparation of sodium and calcium germinates which has proved much more efficient than germa-

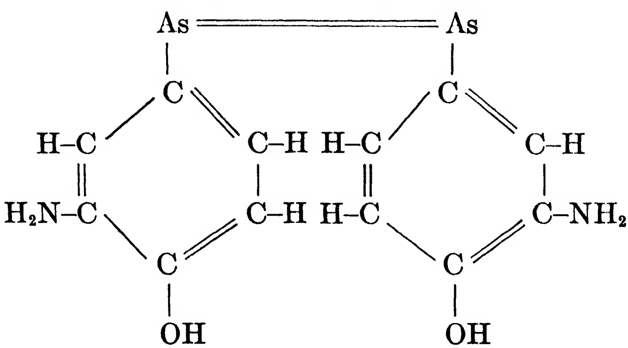
nium oxide in the treatment of pernicious anemia. The germanium salt is only slightly toxic and the results in building up the health of patients seem to be lasting. Several cures which seem to be permanent are reported. Dr. Parr has also experimented with the control of anemia artificially produced in white rats, with positive results.

These results with germanium illustrate how imperfect is our knowledge of the therapeutical value of many elements and compounds whose chemical properties are well known.

VI. Synthetic Medicinals

Certain artificial dyes stain some bacteria and do not stain others. This property has been of very great value to the bacteriologist in the identification of different species of microorganisms. The method is especially valuable in the early and positive diagnosis of diphtheria and tuberculosis.

It has been stated that quinine has a selective germicidal effect upon the organisms which cause malarial fevers and may be administered in sufficient quantities to kill these organisms without killing the patient. These facts suggest the possibility of finding new compounds which will be specific for different diseases. Ehrlich began an intensive study of a series of compounds in the search for a cure for syphilis. He finally, after preparing and testing more than six hundred compounds, decided upon arsphenamine,



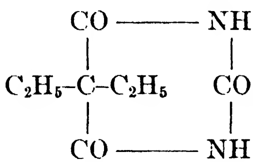
as the most useful. There are some difficulties in the use of arsphenamine, however, and another related compound, neoarsphenamine, $NaOSO_2CH_2NH \cdot C_6H_3(OH)As = AsC_6H_3(OH) \cdot NHCH_2OSO_2Na$, has some advantages.

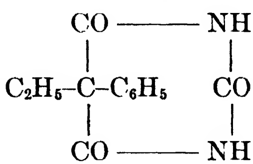
When syphilis has reached the stage of paresis and caused insanity, it has been cured in a considerable number of cases by the use of tryparsamide,

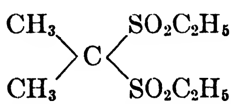
$$H_2NCOCH_2NH \cdot C_6H_4 \cdot AsO(OH)_2.$$

This compound was prepared by Jacobs and Heidelberger at the Rockefeller Institute for Medical Research. Brown and Pearce studied it experimentally with animals, and Lorenz, Loevenhart, Bleckwenn and Hodges developed it successfully in the treatment of paresis. It is reported that it has resulted in the mental restoration of 40 per cent of the patients suffering from paresis, who had been committed to state institutions, enabling them to return to their families and to resume their work, often with increased earning capacity.

During the past seventy years, a large number of other synthetic organic compounds have been introduced successfully into medical practice. Among these may be mentioned:

Barbital (veronal),  , hypnotic.

Phenobarbital (luminal),  , hypnotic.

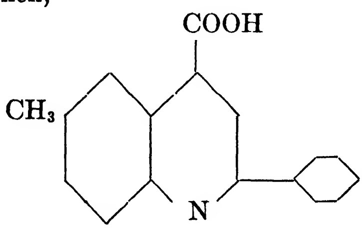
Sulfonal (sulphenmethane),  , hypnotic.

Acetanilide (antifebrine), $C_6H_5NH{-}COCH_3$, antipyretic.

Phenacetin (acetphenetidine), $C_6H_4\langle^{NH-COCH_3}_{O-C_2H_5}$, antipyretic.

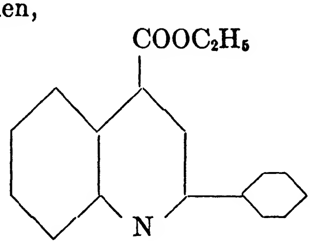
Antipyrine, $\begin{array}{l} CH_3-C-N-CH_3 \\ \quad\ \ \Vert \qquad\quad \rangle NC_6H_5 \\ \ \ H-C-CO \end{array}$, antipyretic.

Cinchophen,



, antirheumatic.

Neocinchophen,



, antirheumatic.

Acetylsalicylic acid, $C_6H_4\langle^{COOH}_{O-COCH_3}$, analgesic or anodyne.

Amidopyrine (pyramidon), $\begin{array}{l} \qquad\qquad\qquad\quad CH_3 \\ \qquad\quad CH-C-N\langle \\ \qquad\qquad\quad \Vert \qquad\quad \rangle N-C_6H_5 \\ (CH_3)_2N-C-CO \end{array}$, antipyretic.

Saccharin (glucidum, U.S.P.), $C_6H_4\langle^{SO_2}_{CO}\rangle NH$, intensely sweet; used by persons suffering from diabetes.

Adrenaline (the hydrochloride, in trade, as epinephrine)

$$\begin{array}{l} \qquad OH \\ \qquad / \\ C_6H_3\text{–}OH \\ \qquad \backslash \\ \qquad CHOH\text{–}CH_2NHCH_3, \end{array}$$ astringent; heart stimulant.

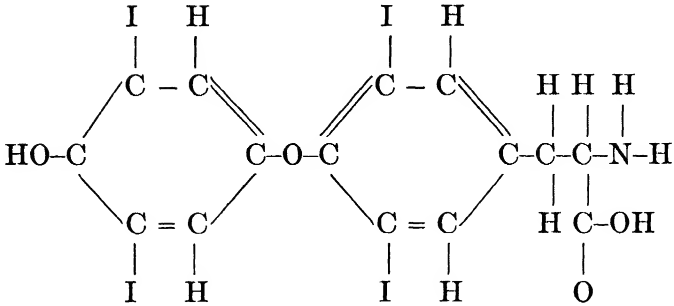
Bayer 205 (Germanin), used in treating sleeping sickness.

Fourneau, 309. A similar or identical remedy prepared by Fourneau at the Pasteur Institute.

Chloramine-T (chlorazene), $$\begin{array}{l} \qquad\qquad\qquad O \\ \qquad\qquad\quad // \\ CH_3\text{—}C_6H_4\text{–}S{=}N\text{–}Cl, \\ \qquad\qquad\quad \backslash \\ \qquad\qquad\qquad O\text{–}Na \end{array}$$ germicide and deodorant.

VII. Hormones

The toxins have been mentioned. These seem to be substances which cause deleterious changes in the fluids of the body. Ductless glands situated in various parts of the body secrete substances which have a beneficent effect. These substances are called hormones. Because of deficiencies in the diet, disease of certain organs, and for other reasons, the glands sometimes fail to function properly and harmful effects follow. It has long been known that persons living in regions where there is no iodine in the potable water used, suffer from goiter. More recently, it was discovered that persons suffering from some forms of goiter are benefited by the administration of an extract of the thyroid glands of sheep or other animals. Still more recently, Dr. E. C. Kendall of the Mayo Laboratory, Rochester, Minnesota, separated a compound called thyroxine, from a very large quantity of the thyroid glands of sheep. Later, Dr. C. R. Harington of England determined the structure of thyroxine and prepared it synthetically. The structure is:



A deficiency in thyroxine causes a decrease in the rate at which food is oxidized and energy produced, i.e., in the rate of metabolism. The administration of one milligram (1/66 of a grain) increases the basal metabolic rate by three per cent. A single dose of this amount will continue to produce its effect for five or six weeks, in a person who has little or no thyroid gland.

Now that the structure of thyroxine is known, it does not seem impossible that some related compound may be prepared synthetically which will perform the same function and which may replace it for therapeutic purposes, somewhat as procaine and butyn have largely replaced cocaine.

The first hormone isolated as a definite chemical compound was epinephrine, frequently called adrenaline. This is dihydroxymethylaminoethylolbenzene, $(HO)_2C_6H_3CHOH \cdot CH_2NH \cdot CH_3$. The natural compound is levorotatory. The racemic form was prepared, synthetically, by Stolz in 1906 and separated into its optical isomers by Flächer in 1908. The natural compound was first isolated from the suprarenal capsules, in the form of a benzoyl derivative, as an active sulfate, by Abel and Crawford in 1897.

So important is this hormone in the animal economy that the removal of both suprarenal capsules from an animal will cause it to die in 24 to 48 hours.

Since its discovery and a careful study of its physiological effects, epinephrine has become one of the most valuable drugs used by physicians and surgeons.

Diabetes is due to a disorganization of the chemical (metabolic) processes by which foodstuffs are utilized in the body for the production of heat and muscular energy. Sugar, instead of being oxidized, accumulates in the blood and is secreted in the urine. Until very recently, the best treatment of diabetes consisted in omitting from the diet sugar and starch which may be converted to glucose by the digestive processes. It is now known that the disease is due to a deficiency in the blood, of a hormone, insulin, secreted by the pancreas. McLeod, and Banting, of Toronto, finally succeeded in preparing an extract from the pancreas which can be injected, intravenously, and which will cause a restoration of the metabolic power of the blood. Unfortunately, this does not remove the cause of the trouble and patients suffering from diabetes must continue the use of insulin through life.

Recently, Abel and Geiling have obtained a crystalline compound which may prove to be the pure hormone.

Hoskins, in an article in *Chemistry in Medicine*, says, "The organs known or believed to secrete hormones are the pineal, pituitary, thyroid, parathyroid, thymus and adrenal glands, together with the pancreas, stomach, upper intestines and the sex glands. Possibly the spleen and liver should be included and the thymus excluded."

The isolation of hormones as pure chemical compounds and their synthesis outside of the animal body is exceedingly difficult because of the very minute quantities found in the animal secretions. In spite of this, the progress already made encourages us to hope for further advances which will add greatly to the resources of physicians in combating disease and maintaining health.

The **proteins** are thought of as more intimately associated with life processes than any other class of compounds. They are very complex compounds, consisting chiefly of carbon, nitrogen, hydrogen and oxygen with a small quantity of sulfur as an essential constituent in most of them and phos-

phorus and small amounts of other elements in some. The essential compounds for the building of proteins are the amino acids, of which amino-acetic acid, $H_2NCH_2CO \cdot OH$, is one of the simplest. About twenty such acids have been prepared by the hydrolysis of proteins. Plants are able to synthesize these amino acids from the compounds of the chemical elements presented to them in nature, especially from carbon dioxide, water, nitrates or ammonia, sulfates and phosphates. Legumes, with the aid of bacteria, can use the atmospheric nitrogen but other plants cannot do this. With few exceptions animals must have the amino acids furnished for their use in the proteins of their foods. Animals fed on proteins which do not contain some of these amino acids will cease to grow or may even die. The proteins of the food are not taken into the blood stream of the animal and built into new tissues directly, but must first be hydrolyzed and broken down to the amino acids of which they are composed by the digestive processes. The animal recombines these acids to form the proteins characteristic of its own body. Emil Fischer showed that the acids condense with themselves and with each other to form polypeptides of the type, $H_2NCH_2CO \cdot NHCH_2CO \cdot OH$.

These facts, in their details, have furnished, during the last thirty years, a new and more scientific basis for the study of problems of nutrition both for the human race and for domestic animals.

VIII. Vitamins

Vitamins are substances found in many of the foods we eat. It has long been known that sailors and others living on a diet without fresh vegetables are liable to be afflicted with scurvy. In the Orient the disease called beriberi has been known since 2600 B.C., but it was not till near the close of the nineteenth century when it was definitely connected, by Dr. Eijkman, with the use of a diet consisting chiefly of polished rice. He observed that chickens developed the

essential features of beriberi when restricted to polished rice as their sole food. The original rice has, in the surface of the grain, a minute amount of a vitamin which will prevent the disease, if it is used with the rice. Soon after this knowledge was gained, beriberi was almost completely eliminated from the Dutch oriental region where Dr. Eijkman was at work.

The isolation of definite chemical compounds which produce the effects ascribed to the vitamin is even more difficult than the isolation of hormones. Recently, some of the vitamins have been isolated and work on this problem is in active progress in a number of laboratories. Thus far the various vitamins have been identified by their physiological effects on animals and man and very few chemical tests for them are known.

Seven fairly well defined vitamins have been discovered:

Vitamin A is found most abundantly in cod-liver oil, butter fat, egg yolk fat, liver, leafy vegetables and yellow pigmented vegetables generally. It does not seem to be found in any vegetable structures which do not contain yellow pigments. At one time it was thought to be possibly identical with carotin, the yellow compound which gives color to carrots but more careful studies have shown that this is not true. This vitamin is readily oxidized at high temperatures but is comparatively stable in the ordinary cooking of food.

The absence of vitamin A in the diet causes injury to epithelial tissues. One method of studying it has been the effects produced in the eyes of rats by its absence from the diet. It is soluble in fats but not soluble in water.

Vitamin B is soluble in water and is, perhaps, more widely distributed than any of the others. It occurs in relative abundance in tomatoes, spinach, legumes, eggs, yeast and glandular tissues, such as the liver and kidney. For adults having a reasonable freedom of choice in the selection of foods, there is little probability of a deficiency. The content

in both human and bovine milk is very variable and is dependent largely on the amount consumed in the food. Foods rich in the vitamin should be included in the diet of nursing mothers. For children artificially fed, the modified milk should be supplemented with something which contains the accessory factor.

Vitamin C is found in fresh vegetables, orange juice, lemon juice, and, especially, tomato juice. It is rather easily destroyed by ordinary processes of cooking but, fortunately, tomatoes lose little of their specific value in the twofold heating of the commercial canning process. The pasteurization of milk destroys a part of the vitamin and scurvy has appeared among infants in France since the introduction of pasteurization. Evidently when pasteurized milk is used, orange juice or tomato juice should also be given. This vitamin is sometimes called the antiscorbutic vitamin, because its absence from the diet causes scurvy.

Vitamin D is found in cod-liver oil in very variable amounts. The amount is increased by exposing the oil to sunlight or ultraviolet light. It has been shown that the compound in the oil which is activated is ergosterol, a sterol found in some fungi. To be effective the light must be of shorter wave-length than $313\mu\mu$. It has been found that 0.000,000,01 gram of vitamin D, synthesized by the action of light on ergosterol, will prevent rickets in a rat.

The beneficial effects of sunlight on children may be partly connected with the development of this vitamin. It is well to remember, however, that sunlight has a powerful bactericidal effect.

In the absence of vitamin D, calcium and phosphorus are not properly utilized in the formation of bones, with the result that rickets develops.

Vitamin E is the antisterility factor. Animals deprived of it lose the power of reproduction. The effects differ in the two sexes. In the female, ovulation remains unimpaired and the ova may undergo fertilization, but the embryos die and

are re-absorbed before they reach maturity. In the male, absence of the factor from the food leads to degeneration of the sperm cells.

Vitamin E occurs in green leafy vegetables, in cereal grains, and in certain oils, notably in those of the wheat germ, hemp seed and yellow corn. It appears to be entirely absent from cod-liver oil.

At the present time no data are available demonstrating that it plays a rôle in human reproduction. It seems not unreasonable to assume that it does. The wide distribution of the vitamin appears to justify the belief that a deficiency of it in man is very improbable.

Vitamin $G(B_2)$ is a water soluble substance often found associated with vitamin B. The two were separated and distinguished with difficulty but their difference is now well established and the ratio between B and G varies in different foods. Milk, eggs, meat and fish contain vitamin G and ox liver and yeast are rich in it. The absence of vitamin G is thought to be the cause, or a chief cause, of pellagra and the vitamin has sometimes been called "pellagra-preventive" (P–P).

The study of the vitamins has demonstrated that a diet which will maintain health and the proper functions of the body must contain minute amounts of other compounds in addition to proteins, furnishing the necessary amino acids, salt and other mineral constituents, and enough carbohydrates or other compounds to supply heat and muscular energy. During the last thirty years, the study of the amino acids and of the vitamins has contributed more than anything else toward placing dietary rations on a scientific basis.

IX. Heat and Energy in the Human Body

More than thirty years ago, Atwater and his colleagues demonstrated that, within the experimental error (not exceeding one per cent), the heat generated by the oxidation of

food in the human body is the same as that produced by burning the same food in a calorimeter. They also showed that a person performing muscular work oxidizes a much larger quantity of food. Only a part of the energy from the increased oxidation is converted into mechanical energy. Athletes may convert as much as 33 per cent of the energy from the extra oxidation to mechanical energy. Ordinarily 18 to 23 per cent is common. This compares favorably with the efficiency of a very good steam engine. A good locomotive gives 10 per cent; a Diesel engine may give 40 per cent.

The body is not a heat engine in the ordinary sense, however. It is well known that the limit of efficiency for a steam engine or any other device by which heat is converted to mechanical energy is proportional to the difference between the temperature of the steam entering a steam turbine, and the temperature of the steam leaving its vanes, divided by the absolute temperature of the steam as it enters. Thus if the steam entering the turbine has a temperature of 150° and a temperature of 70° when it leaves, the greatest possible efficiency of the engine for the conversion of heat to mechanical energy is 150–70/423, or 18.9 per cent. Since the muscles do their work at a practically constant temperature, it is evident that the energy of the food is not converted into heat before it is converted to mechanical energy.

The only known method of converting chemical energy in quantity, into mechanical energy, while working at a nearly constant temperature, is a primary electrical battery. It is possible that muscles work with the aid of electrical forces but no convincing evidence of this has been found. It seems, on the whole, most probable that muscular tissues convert chemical energy directly into the mechanical energy of muscular contraction. A first step toward the solution of this riddle has been made by Fletcher and Hopkins in England and by Embden, Hill and Meyerhof in Germany. A distinction has been made between the heat evolved during the contraction of a muscle and the brief

period of recovery which follows. The first appears when the muscle is in an atmosphere of nitrogen and evidently is not dependent on oxidation by the oxygen of the air, while the second appears in the presence of oxygen, only. In the absence of oxygen, lactic acid accumulates in the muscle while in the presence of oxygen it does not. The most recent studies indicate that on stimulation of vertebrate muscle phosphocreatine breaks down forming phosphoric acid and creatine. Energy is liberated, some of which is used in the contraction of the muscle. Lactic acid forms in a period some seconds after the phosphocreatine breaks down. It appears that the energy liberated by the formation of lactic acid is partly used in the synthesis of phosphocreatine. In the absence of oxygen, lactic acid accumulates in the muscle, while in the presence of oxygen it tends to disappear. In the presence of oxygen the lactic acid is resynthesized to glycogen, the energy required being produced by the oxidation of some carbohydrate materials. The mechanism of the conversion of chemical energy to mechanical energy remains as much in the dark as ever but it is certain that such a transformation occurs and that it takes place in accordance with the law of the conservation of energy.

Atwater and his associates were unable to show that a person engaged in active mental work uses any more chemical energy than the same person at rest. Very recently, however, Benedict has been able to demonstrate that a very small expenditure of chemical energy accompanies mental work. This must mean that increased metabolism in the brain accompanies mental activity. The amount of energy involved is very small.

Many other illustrations might be given of the methods by means of which chemistry and bacteriology are giving us a constantly increasing control of the causes of disease and methods of curing diseases which have attacked the human organism. The progress of the last seventy-five years exceeds the progress of medicine during fifty centuries before

that time. In Geneva, during the sixteenth century, a child lived, on the average, 21 years. In 1921 he lived, on the average, 58 years. Statistics seem to show, however, that the expectation of life for a person 50 years of age has been scarcely increased. It seems probable that the effects of improper diet, increased mental strain and wrong habits become increasingly potent after that age, when the natural recuperative powers of the organism grow less.

X. Sociological Difficulties

Every endeavor should be made further to increase our knowledge. It is evident that we are still profoundly ignorant about many things of great importance in connection with disease and nutrition. For the race as a whole, however, there is much greater need to use the knowledge we have than to increase its amount. The nation and states will spend millions of dollars to prevent diseases which threaten hogs or cattle but will use only a small fraction of the same amounts in supporting well-trained health officers who might do a vast deal to prevent disease among human beings. A few years ago misguided and misinformed persons secured the repeal of the law for compulsory vaccination in California. Since then the disease has increased 800 per cent in the state. The hookworm disease can be cured and prevented and is now largely controlled in the United States, but is has proved to be a very difficult problem to overcome the ignorance and superstition of Oriental peoples where the hookworm is prevalent. Sociological and international problems connected with the health of races are even more difficult than those of medicine.

References

Vallery. *Life of Pasteur*. New York: Doubleday, 1927.

Stieglitz, Julius, ed. *Chemistry in medicine*. New York: Chemical Foundation.

Wells, H. Gideon. *The chemistry of immunity*. Second Edition, 1929. New York: Chemical Catalog Co. American Chemical Society Monographs.

SHERMAN, H. C. *Vitamins*. Second edition. New York: Chemical Catalog Co., 1931. American Chemical Society Monographs.

ROSE, W. C. "Dietary facts and fads." *Ind. and Eng. Chem.*, 1931, **23**, 711.

HILL, A. V. "Muscle metabolism." *Physiol. Rev.*, 1932, **12**, 56.

MEYERHOF, O. *Die chemischen Vorgänge in Muskel*. Berlin: Julius Springer, 1930.

CHEMICAL ABSTRACTS and the various journals cited in the abstracts on Biological Chemistry.

INDEX

INDEX

THIS BOOK

MODERN ALCHEMY

was set, printed and bound by The Collegiate Press of Menasha, Wisconsin. The cover design is by The Fox Studio of Springfield, Illinois. The type face is 11 on 13 Monotype 8A and 25J. The type page is 24 x 41 picas. The text paper is 70 pound White Valley Offset. The end sheets are 80 pound White Schuylkill. The jacket is 20 x 26-50 Blue Antique Albemarle. The binding is Saylrock Red No. 222.

With THOMAS BOOKS careful attention is given to all details of manufacturing and design. It is the Publisher's desire to present books that are satisfactory as to their physical qualities and artistic possibilities and appropriate for their particular use. THOMAS BOOKS will be true to those laws of quality that assure a good name and good will.